

**A FUNDAMENTAL STUDY OF THE MECHANISMS  
OF ACTION OF POLYMERS AS RETENTION  
AND DRAINAGE AIDS**

**Project 3276**

**Report Two  
A Progress Report  
to  
MEMBERS OF PROJECT 3276**

**October 6, 1976**

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

A FUNDAMENTAL STUDY OF THE MECHANISMS OF ACTION OF  
POLYMERS AS RETENTION AND DRAINAGE AIDS

Project 3276

Report Two

A Progress Report

to

MEMBERS OF PROJECT 3276

October 6, 1976

MEMBERS OF PROJECT 3276

Member companies of The Institute of Paper Chemistry and the following nonmember companies who have contributed to the support of the project are:

BASF Wyandotte Corporation

Buckman Laboratories, Inc.

Container Corporation of America

Englehard Minerals and Chemicals Corporation

General Mills Chemicals, Inc.

Monsanto Industrial Chemicals Co.

National Starch and Chemical Corporation

# TABLE OF CONTENTS

	Page
SUMMARY	1
INTRODUCTION	3
RETENTION STUDIES	5
Precision of Retention Determination with the Rapid Mixing Apparatus (RMA)	5
Effect of Pulp Classification	9
Effect of Pulp Fibrillation	15
Effect of Sheet Basis Weight	19
Effect of Polymer Dosage	23
Conclusions	32
DRAINAGE STUDIES	33
Constant-rate Filtration Measurements	33
Effect of Polymer Structure on Drainage	33
Effect of Pulp Fines on Drainage	34
Effect of Drainage Aids on Wet Pressing	47
Experimental	47
Results and Discussion	50
Measurement of Drainage Times on the Rapid Mixing Apparatus	52
Experimental	52
Results and Discussion	54
Conclusions	59
FUTURE WORK	61
ACKNOWLEDGMENTS	63
LITERATURE CITED	64

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

A FUNDAMENTAL STUDY OF THE MECHANISMS OF ACTION OF  
POLYMERS AS RETENTION AND DRAINAGE AIDS

SUMMARY

This progress report describes our continuing efforts to better understand the mechanisms by which polymers mediate enhanced drainage and retention. This information is necessary to the papermaker and the chemical supplier in order to use these expensive materials more efficiently and to identify those aspects of the polymer structure which make it effective.

A series of studies of retention of  $\text{TiO}_2$  in sheets was carried out using the Rapid Mixing Apparatus. A wide range of polymer dosages from 0.0025 to 0.5% based on o.d. pulp encompassed the span over which the polymers were effective. It was shown that the better retention aids produced a large proportion of the retention of  $\text{TiO}_2$  to the fibers prior to sheet formation and also effected good pulp fines retention during drainage.

Investigations with pulps beaten to different degrees indicated that increased refining produced increased retention in direct proportion to the hydrodynamic specific surface area. The increase in retention is a result of the increased number of collisions/unit time of filler particles with fibrous material. The presence of pulp fines also increases retention by increasing the collision rate.

It was demonstrated for the first time that both charge neutralization (or electrostatic patch) and bridging mechanisms can contribute separately to the retention of filler. This behavior was found only for high molecular weight polymers. Those of moderate molecular weight enhanced retention by a charge

neutralization mechanism only. A low charge density appears to enhance the bridging ability of a high molecular weight polyelectrolyte more than does a high charge density.

Constant rate filtration measurements of pulps treated with various drainage aids indicated that only those polymers with high molecular weight were appreciably effective. As with retention, a polyelectrolyte with low charge density provided the greatest improvement in drainage.

Increased drainage was found to correlate most strongly with the reduction in hydrodynamic specific surface area caused by the polymer. The drainage aids produced negligible changes in swollen specific volume and compressibility.

Analysis of a series of furnishes with increasing fines contents showed that most of the decrease in hydrodynamic specific surface area could be attributed to that associated with the fiber surface, rather than with the fines.

The effect of drainage aids on water removal in wet pressing was investigated with the press in the IPC High Speed Wet End. Although the experimental precision was only fair, improved dewatering (by about 1% moisture) could be demonstrated with the use of some drainage aids. In some cases polymers which increase drainage on the wire may be ineffective in the press section.

The Rapid Mixing Apparatus was modified to permit measurement of an average drainage time during sheet formation. Thus, both retention and drainage can be monitored concurrently during the same experiment. Preliminary results suggest that polymer bridging is the major mechanism of action by the drainage aid.

A good correlation was found between Canadian standard freeness and filtration resistance. This suggests that the former simple measurement can provide useful measures of drainage properties.

## INTRODUCTION

Recent (sometimes heated) discussions at TAPPI meetings concerning application of polymers at the wet end, and the interest shown in the TAPPI short courses on retention and drainage, reveal the importance of these topics to the paper industry. This project was initiated to improve our understanding of how polymeric retention and drainage aids function. This knowledge will permit their most effective utilization.

The work described in this report focuses on the first two phases (1) of the project. These are:

- I. Mechanisms of filler and fines retention by polymers, and
- II. Mechanisms of drainage enhancement by polymers.

In the previous work on this project (1) experiments at short contact times showed that nonequilibrium flocculation was an important contributor to the retention process. This phenomenon is greatly enhanced by the use of high molecular weight polymers. It was also shown that a long chain length of the polymer was necessary for the effective retention of pulp fines under sheetmaking conditions. The benefit of having a low charge density on the polymer was noted and was attributed to the enhanced possibilities for bridging to other surfaces which the longer loops of such an adsorbed macromolecule could provide. The rate-determining step in the retention process was found to be the coflocculation of the filler with the fines. It is governed by the efficiency of the collisions between these two entities, which in turn is a function of the mediating polymer's charge, dosage, and molecular weight.

Exploratory experiments were described (1) concerning the use of constant rate filtration measurements to assess the effect of polymers on the drainage

properties of a pulp. It was shown that polymers could enhance the drainage of classified as well as whole pulps. This suggested that flocculation of fines onto the fibers may not be the most important mechanism of drainage improvement with whole pulps.

In the first part of this report the continued probing of the interactions between polymers and the basic components of a furnish (fiber, fines, and filler) is described. The near-ideal mixing conditions of the Rapid Mixing Apparatus are used to examine the effects of a number of commercially important operational parameters on filler retention.

In the second part of the report the influence of drainage aids on the pulp hydrodynamic properties as determined from constant rate filtration measurements is described. The separate contributions of fibers and fines are delineated.

Limited studies of the effect of drainage aids on wet pressing were carried out with the press section of the IPC High Speed Wet End.

A description of a modification of the Rapid Mixing Apparatus (RMA) to permit concurrent measurements of drainage and retention is presented. Some exploratory runs are included.

Finally, the work proposed to complete Phases I and II is outlined.



## RETENTION STUDIES

PRECISION OF RETENTION DETERMINATION WITH THE RAPID  
MIXING APPARATUS (RMA)

Some limited studies of replication of retention results within a given run were reported previously (1). We wanted to extend these findings to encompass the variables of polymer concentration and pulp fines content and to examine the variability among replicate runs.

A series of runs was carried out using Q100 (a high-charge density, high-molecular weight cationic polyelectrolyte) as the retention aid and  $\text{TiO}_2$  (1) as the filler. The two pulps, No. 3 whole (340 ml CSF) and No. 3 classified (605 CSF), have been described previously (1); their use allowed the effect of freeness and pulp fines content to be evaluated. Sheets of about 60 g/m<sup>2</sup> basis weight were formed with the RMA in the sheet mold mode as detailed in Report One (1).

For the present experiments a "run" consists of the formation of a series of sheets from stock consisting of a single 30 g batch of disintegrated pulp with 5% (based on the o.d. pulp)  $\text{TiO}_2$  added. The stock was treated with the polymer in the RMA at a series of dosage rates from 0.0025 to 0.5% (based on o.d. pulp). The concentration of polymer in Reservoir II at the beginning of a run was that necessary to give the lowest dosage rate. During the run it was raised incrementally ten times to give a total of eleven dosage levels. Both pulp and polymer solution were adjusted to pH 5 with  $\text{H}_2\text{SO}_4$  for all experiments in this report. At each concentration level four sheets were made: two each at two contact times, 7.9 and 40 seconds. The two sheets at a given contact time and concentration were combined to increase the sample size and thereby the

precision of the ashing analysis. Based on the results reported earlier (1), the two contact times were chosen as representative of characteristic points in the typical course of the development of retention with increasing contact time. The shorter time (7.9 sec) is of the order of that on high-speed paper machines where the polymer is added at the fan pump or the final screens. Depending on the particular polymer the level of retention at this contact time may either be near or substantially less than the maximum value reached at long times. The longer time (40 sec) was chosen to give degrees of retention indicative of the maximum.

Either three or four runs were made with each of the two pulps. The results are presented in Fig. 1 (No. 3 whole pulp) and 2 (No. 3 classified pulp). The points from particular runs are not identified. As a measure of the experimental precision a standard deviation,  $\sigma$ , was defined as follows:

$$\sigma = \left[ \sum_i \sum_j (R_{ij} - \overline{R_j})^2 / (n-1) \right]^{1/2} \quad (1)$$

where

$R_{ij}$  = the percentage retention of run i at polymer concentration j, and

$\overline{R_j}$  = the average of the k runs of the retention at polymer concentration j, or

$$\overline{R_j} = (1/k) \sum_{i=1}^k R_{ij}$$

n = the total number of retention values being considered.

The standard deviations in units of percentage retention for the various sets of data are listed in Table I.

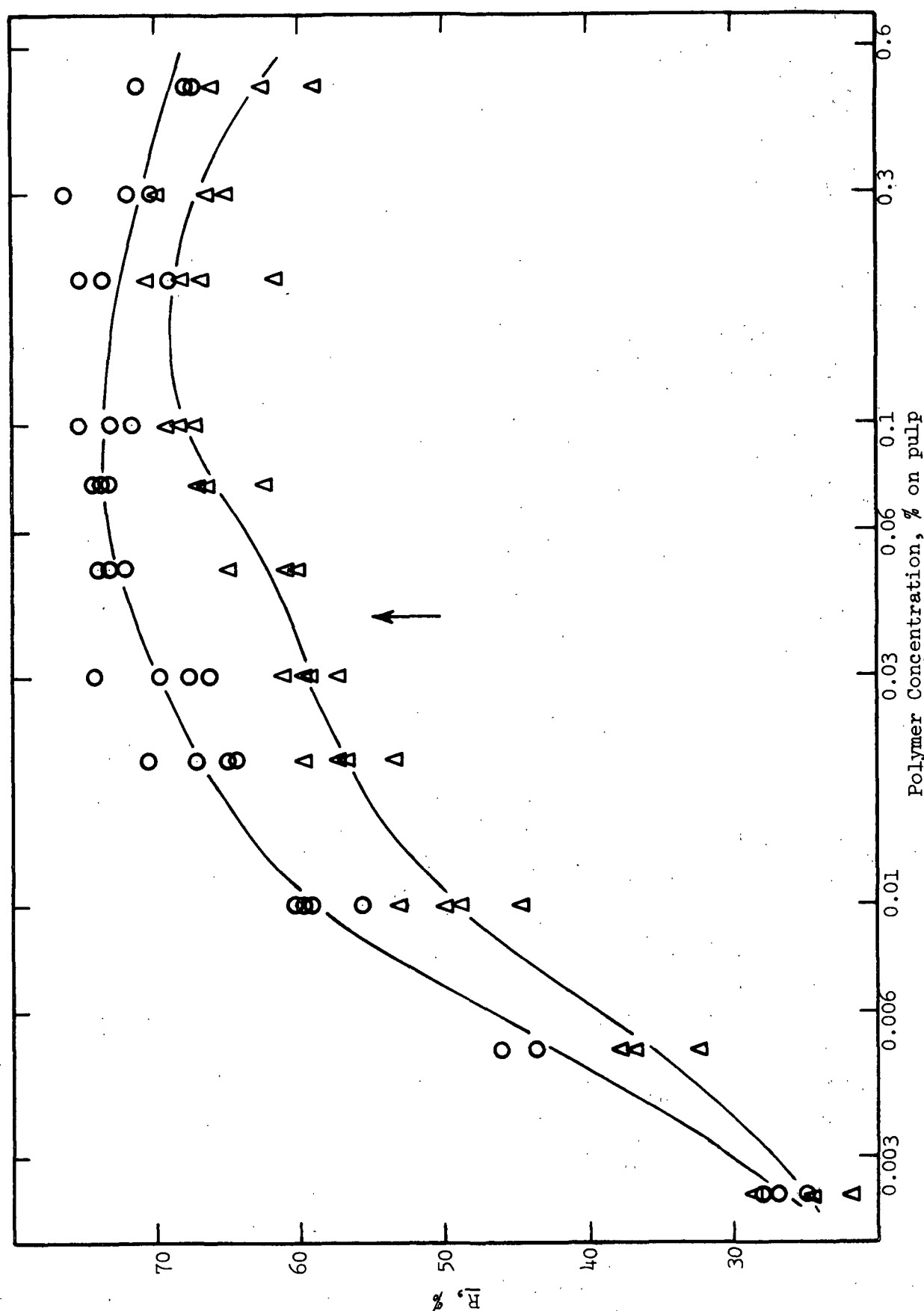


Figure 1. Check of Reproducibility of Retention Determination. Polymer: Q100. Pulp: No. 3 Whole.  
Contact Time: Circles, 40 sec; Triangles, 7.9 sec. Arrow Indicates Concentration at Zero Zeta Potential

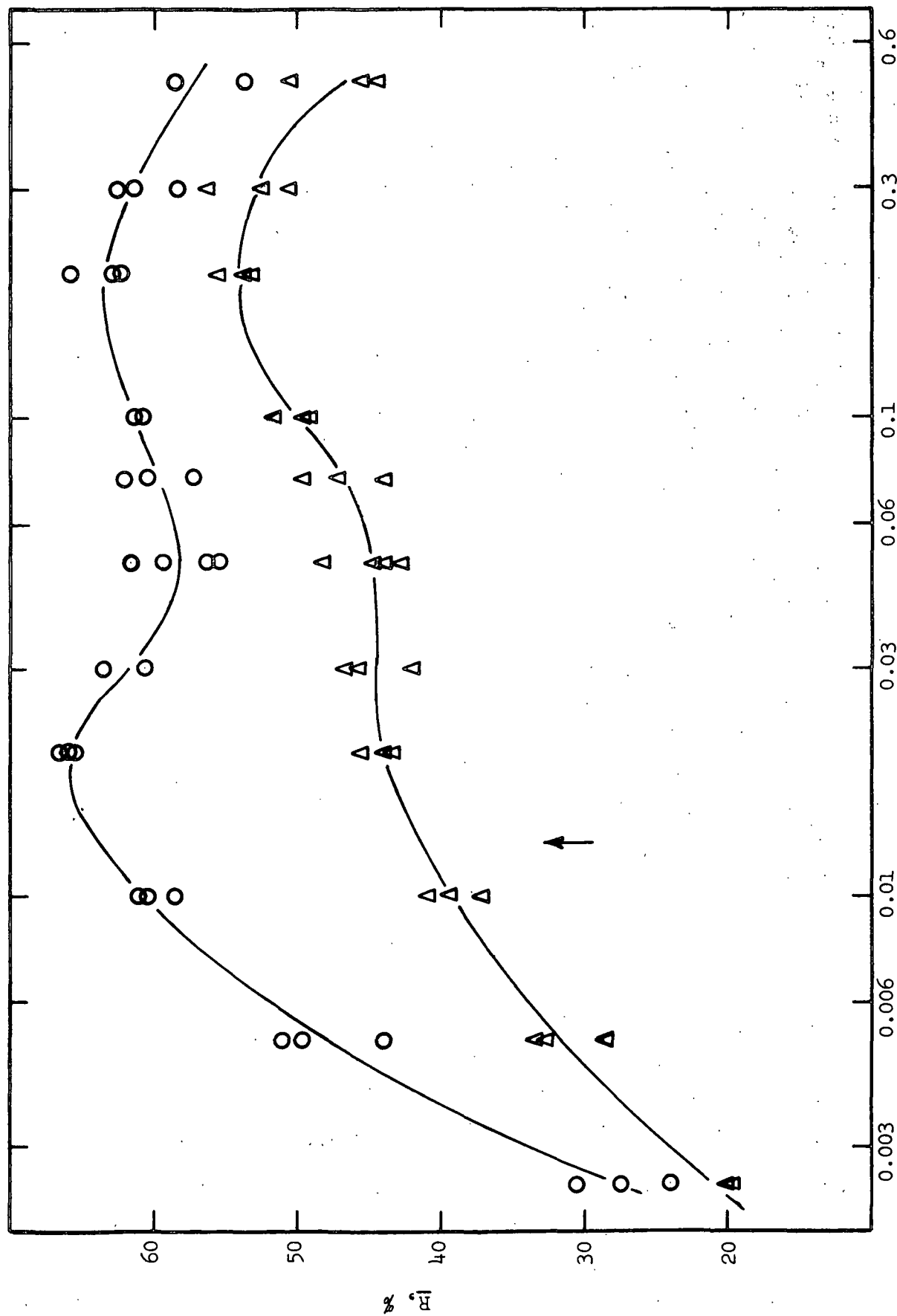


Figure 2. Check of Reproducibility of Retention Determination. Polymer: Q100. Pulp: No. 3 Classified.  
Contact Time: Circles, 40 sec; Triangles, 7.9 sec. Arrow Indicates Concentration at Zero  
Zeta Potential

TABLE I  
STANDARD DEVIATIONS OF RETENTION VALUES

Pulp	Contact Time, sec	<u>n</u>	$\sigma$ , %
No. 3 whole	7.9	37	2.4
"	40.0	37	2.4
No. 3 classified	7.9	34	1.9
"	40.0	33	2.0

If all 141 values are considered together, their standard deviation is 2.2%. Examination of the data in Fig. 1 and 2 reveals the experimental scatter to be random with no obvious dependence on contact time or polymer concentration. [The latter is implicitly assumed in the use of Equation (1).] The results in Table I suggest that the precision using the classified pulp is a little better than that for the whole pulp, and that overall the reproducibility between runs is very good.

The solid lines in Fig. 1 and 2 are smoothed curves drawn through the  $\overline{R}_1$  values (the latter not shown). These smoothed curves will be used to represent the data for these polymer/pulp systems in a number of subsequent plots in this report.

#### EFFECT OF PULP CLASSIFICATION

In order to investigate further the role of pulp fines on the retention process, a series of runs was carried out using pulps No. 3 whole and No. 3 classified. The latter was prepared (1) from the former by two passes over a  $70 \times 48$  mesh wire on the IPC Web Former and should contain very few fines. It is possible (2) that some irreversible drying of the classified pulp occurred during the

dewatering process so that its degree of surface fibrillation may be slightly less than that of the whole pulp. This will not affect the conclusions to be drawn here.

Runs were made on the two pulps with Q100, T100 (a moderately high-charge density, medium-molecular weight cationic polyelectrolyte), and Q5 (a low-charge density, high-molecular weight cationic polyelectrolyte) as the retention aids. As mentioned in the previous section two levels of contact time were employed with polymer dosage as the major variable. Representative results are shown in Fig. 3 and 4 for Q100. The smoothed curves are taken from Fig. 1 and 2 and are replotted to facilitate comparison of the effect of pulp type on retention. It is evident that considerably enhanced retention is achieved with the whole pulp in the range of commercial dosage rates ( $0.5-2 \text{ lb/ton} = 0.025-0.1\%$ ). The difference is less at the longer contact time and may decrease still more at yet longer contact times (see below).

Comparison of the retention properties of whole and classified pulps using T100 and Q5 gave similar results. That is, the whole pulp yielded higher retention of  $\text{TiO}_2$  than the classified pulp, with the difference decreasing at longer contact times. Note that at the concentrations for maximum retention of Q100 and also of the high-molecular weight Q5, the zeta potentials are strongly positive. This is in accord with other findings (1,3).

It is reasonable to suppose that the enhanced retention with the whole pulp is a result of the important role of fines in the retention process. Because of their small mass, the fines will participate in many more collisions with  $\text{TiO}_2$  particles per unit time than will the larger fibers. The large specific surface area of the fines compared with that of the (fibrillated) fibers will further accentuate the ability of the fines to "adsorb"  $\text{TiO}_2$  during a limited time span.

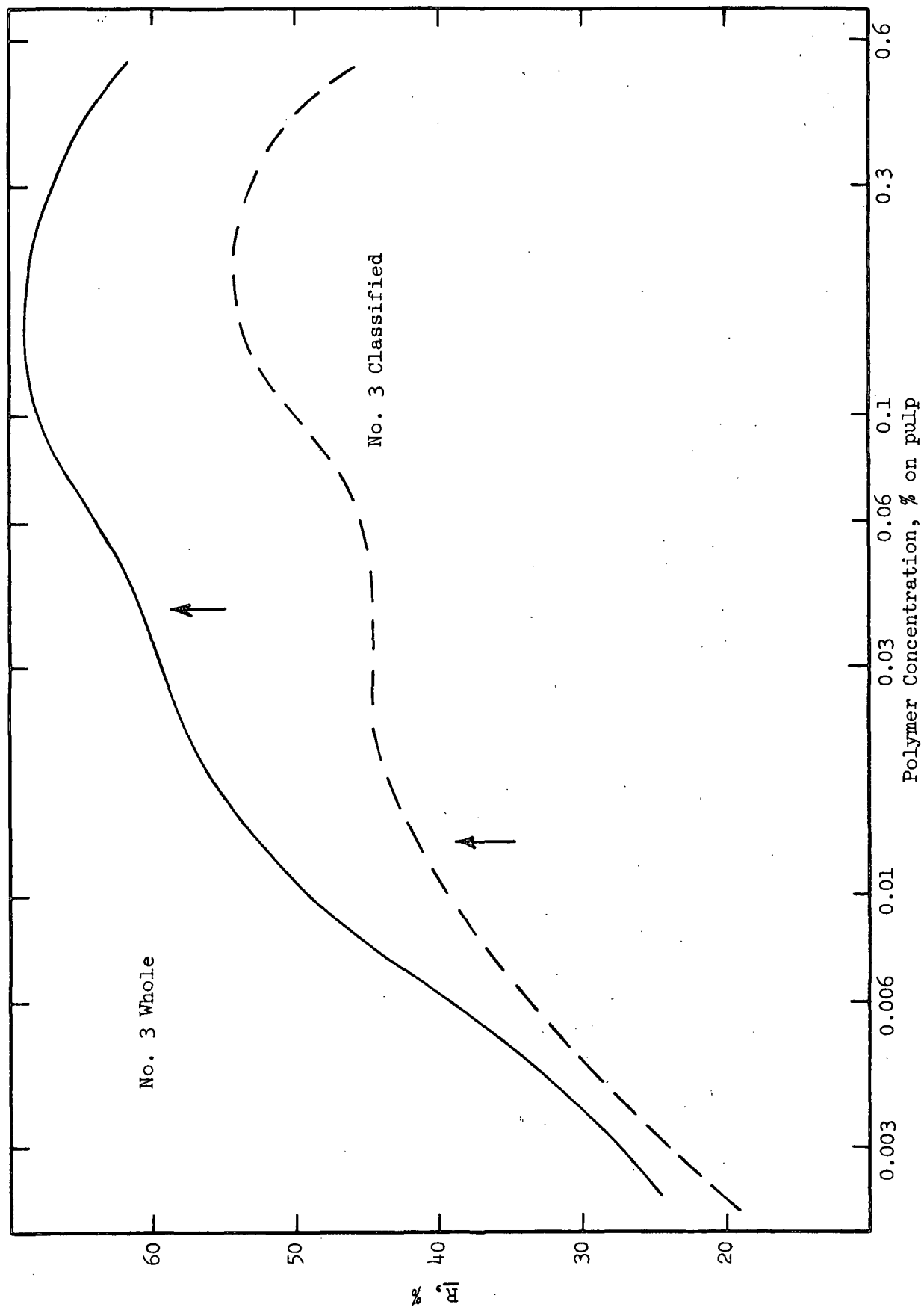


Figure 3. Effect of Pulp Classification on Retention. Polymer: Q100. Contact Time: 7.9 sec.  
Arrows Indicate Concentrations at Zero Zeta Potential

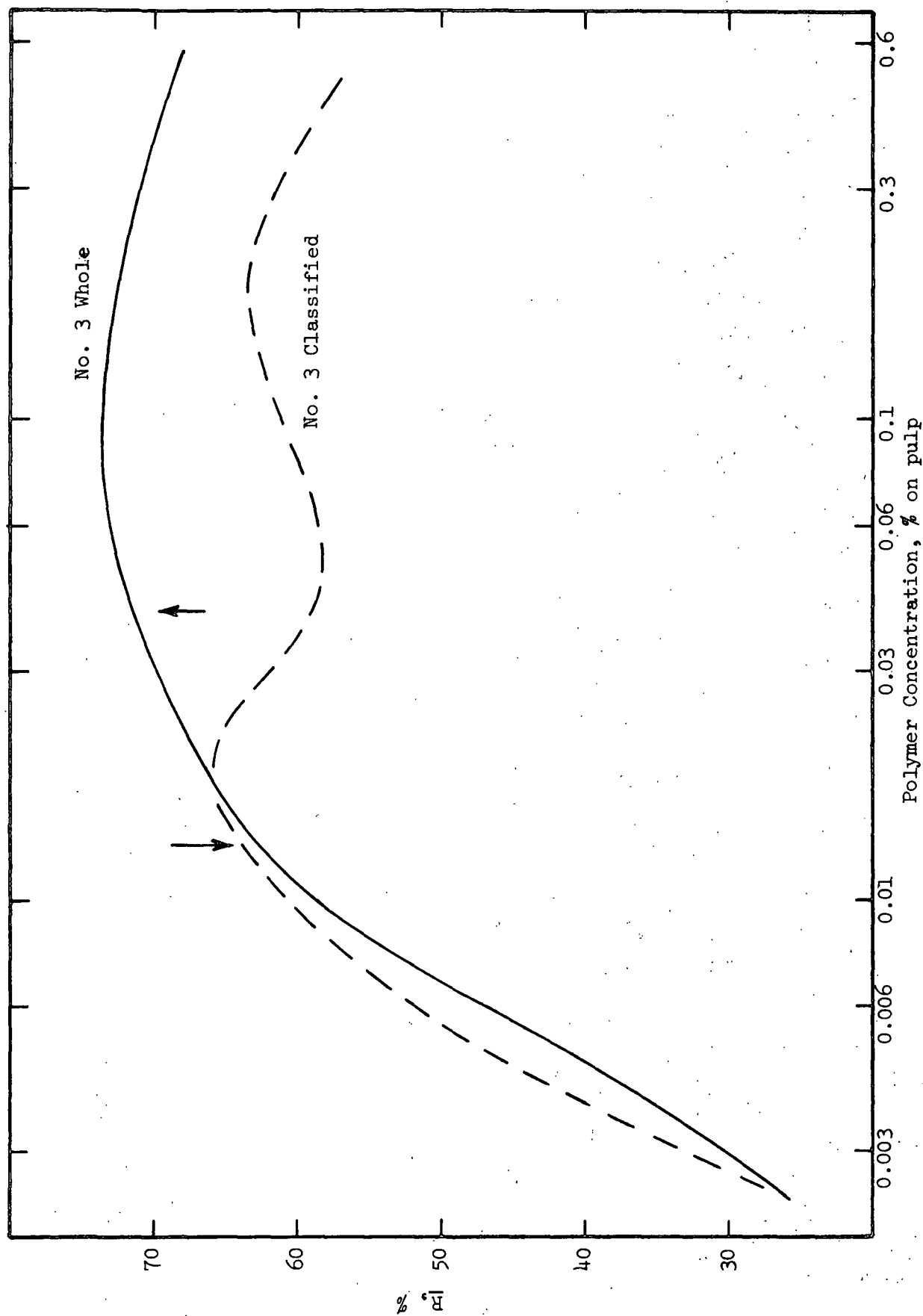


Figure 4. Effect of Pulp Classification on Retention. Polymer: Q100. Contact Time: 40 sec.  
Arrows. Indicate Concentrations at Zero Zeta Potential



The fines with  $\text{TiO}_2$  may then be retained by the fibers either before or during sheet formation.

A striking illustration of the fines effect is shown in Fig. 5 for Q5 at a concentration of 0.1%. This dosage provides the maximum retention for both whole and classified pulp at both 7.9 and 40 seconds contact time. The plot in Fig. 5 shows retention as a function of contact time for the two pulps. Contact times less than 1 sec were obtained with the moving wire mode (1) of the RMA while the longer contact times were obtained with the sheet mold mode. Again, the utility of the fines for enhancing retention at both the very short and intermediate times is evident. However, at long times ( $\sim 90$  sec) the differences between the two pulps (with respect to degree of retention) vanish. The much higher collision rate of the fines with the  $\text{TiO}_2$  allows the maximum retention for the whole pulp to be reached in  $\sim 10$  sec at which time the classified pulp shows only 60% retention. The fact that the classified sample eventually attains a very high level of retention (in the absence of fines) is attributed to the strong bridging ability of this polymer sample.

A prime factor in the level of retention reached by the various pulps is the contact time. The more fundamental parameter underlying this factor is the collision rate of the various species in the furnish. Better means for determining this parameter under mill conditions (that is, defining the degree of agitation after the point of addition and through the headbox) must be sought, so that results such as those above can be applied to the paper machine.

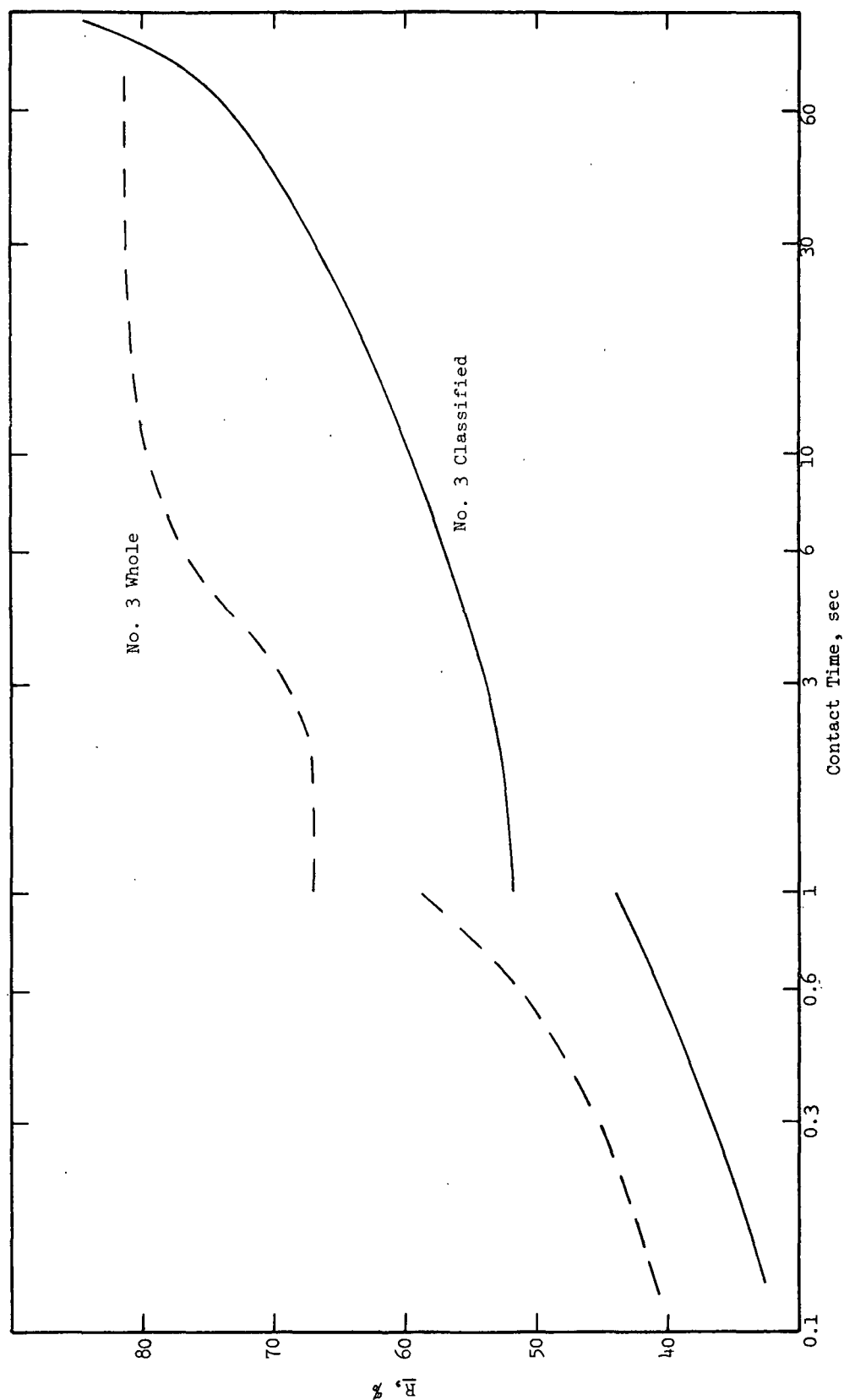


Figure 5. Effect of Pulp Classification on Retention. Polymer: Q5.  
Polymer Concentration, 0.1%

## EFFECT OF PULP FIBRILLATION

It was seen in the previous section that there was a respectable amount of filler retention even with a classified pulp. It might be expected that such behavior would be a strong function of the degree of surface fibrillation of the pulp since it has been observed (4) that much of the retained  $TiO_2$  is caught on the microfibrils rather than on the underlying fiber surface for the case of simple coflocculation with no polymeric additives.

To evaluate this hypothesis, we made a series of runs using T100 as the retention aid and three pulps prepared by classifying pulps beaten from a single stock (bleached kraft softwood) to different levels of freeness (1). The three pulps, No. 1 classified, No. 3 classified, and No. 4 classified, had freenesses of 735, 605, and 515 ml CSF, respectively. The results are presented in Fig. 6 and 7 as percentage retention versus polymer dosage for 7.9 and 40 seconds contact time, respectively. It is manifest that increased fibrillation resulting from the beating process has produced increased retention at both contact times and all polymer dosage levels. Two salient points are to be noted. The polymer dosage for maximum retention is very low ( $\sim 0.01\%$ ), and the corresponding zeta potential is near zero. Further discussion of these points will be deferred to a later section.

To obtain a quantitative measure of the effect of fibrillation, the values of maximum retention in Fig. 6 and 7 have been plotted against the hydrodynamic specific surface areas,  $S_w$ , of the various pulps (5) in Fig. 8. Linear least squares fits (shown) to the two sets of data gave correlation coefficients for the short and long contact times of 0.99 and 0.95, respectively. The slopes indicate the increase in retention due to the increased fibrillation. The

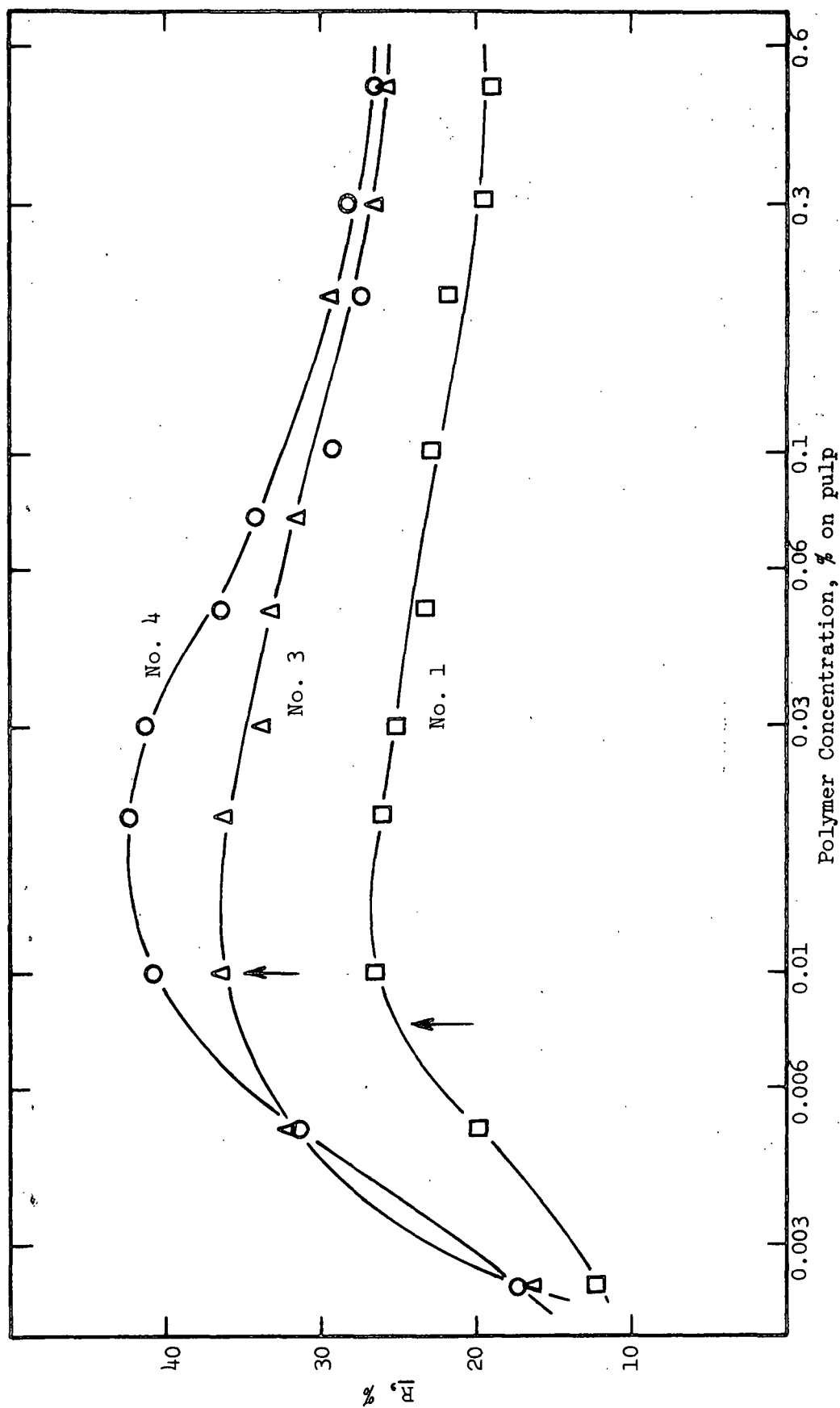


Figure 6. Effect of Surface Fibrillation on Retention with Classified Pulps. Polymer: T100.  
Contact Time: 7.9 sec. Numbers Denote the Pulp. Arrows Indicate Concentrations  
at Zero Zeta Potential

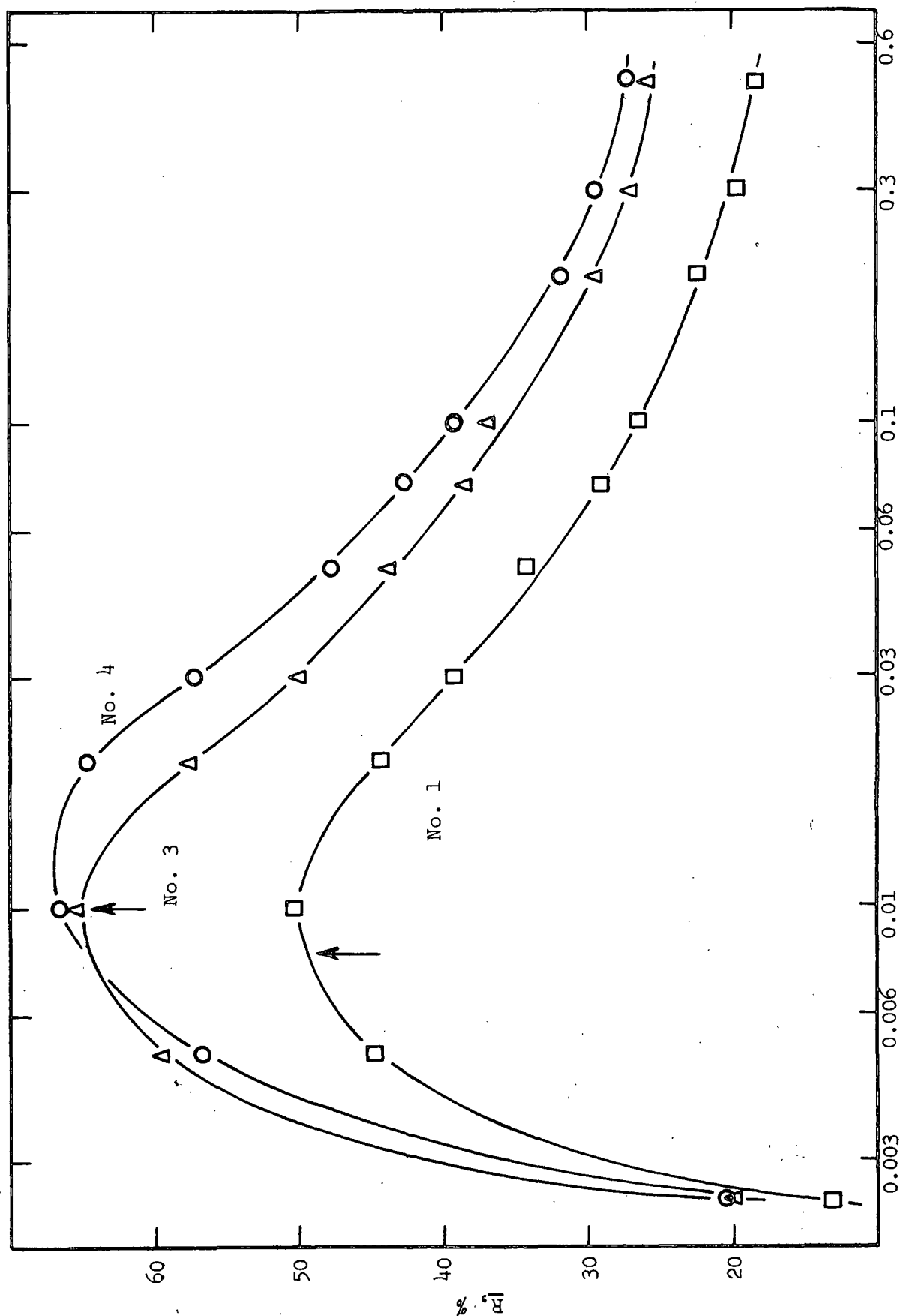


Figure 7. Effect of Surface Fibrillation on Retention with Classified Pulps. Polymer: T100. Contact Time: 40 sec. Numbers Denote the Pulp. Arrows Indicate Concentrations at Zero Zeta Potential

similarity in slopes for the two contact times provides further evidence that the increase in retention with time is a function of the number of collisions between  $\text{TiO}_2$  and reactive surfaces. Similar slopes to these from equivalent experiments using Q100 with classified pulps No. 1 and 3 reinforce this view. Although the evidence for a linear relationship (Fig. 8) appears reasonable, it is possible that over a broader range of variables nonlinearity would ensue.

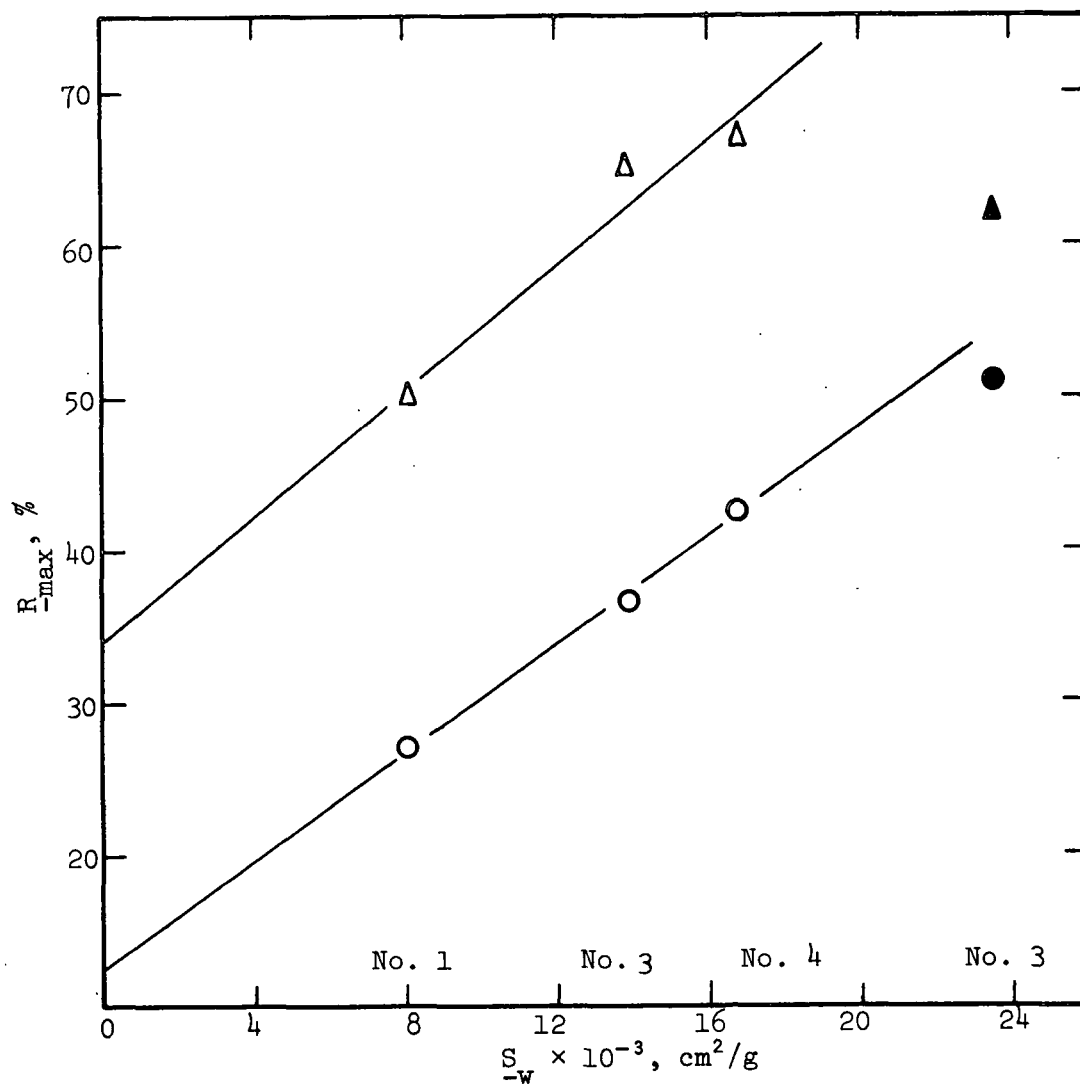


Figure 8. Variation of Maximum Retention with Hydrodynamic Specific Surface Area. Contact Time: Triangles, 40 sec; Circles, 7.9 sec. Pulps: Open Symbols, Classified; Closed Symbols, Whole. Numbers Denote the Pulp

The intercept at  $S_{-w}$  equals zero is meaningless. Pulp No. 1 classified was not beaten but undoubtedly possessed some fibrillation due to pulping and slushing operations. Therefore, the minimum value of retention at a given contact time occurs at a value of  $S_{-w}$  corresponding to smooth, unfibrillated fibers and lies slightly to the left of the data for No. 1 classified pulp.

It is of interest to compare the results of the same polymer on a whole pulp, No. 3. The corresponding values are shown as filled symbols in Fig. 8. For a whole pulp there is competition between (fibrillated) fibers and fines for the  $TiO_2$ . Subsequently, some of the fines may be retained by the fibers. Apparently at the lower level of retention (short contact time) sufficient fines are retained so that the level of retention nearly corresponds to that expected for the measured  $S_{-w}$ , the latter now containing contributions from both fibers and fines. However, at the longer contact time a large proportion of the  $TiO_2$  is associated with those fines which are not retained by the sheet with a resulting low value for retention. This conclusion is in agreement with the finding in Report One that T100 was not effective in retaining fines.

#### EFFECT OF SHEET BASIS WEIGHT

Retention of filler can occur either prior to or during drainage on the wire. The employment of polymers giving tenacious flocculation is designed to maximize the former. That part of the retention occurring during sheet formation is a combination of mechanical sieving of the filler by the web and capture by the fibers of the particles as they make their tortuous way through the web. For  $TiO_2$  (0.15  $\mu m$  in diameter) sieving is not important unless the filler is attached to a large pulp fine.

A series of experiments was carried out to separate the contributions to retention occurring before and during sheet formation. Whole pulp No. 3 was treated with various dosages of Q100, and retentions were measured after contact times of 7.9 and 40 sec. Sheets of three different basis weights were made by varying the setting of timer T1 (see Report One) regulating the amount of furnish delivered to the decklebox. The consistency in the decklebox was kept constant at 0.25%, and a constant suction (10 inches Hg) was employed.

The results are shown in Fig. 9 plotted as percent retention against polymer dosage at a contact time of 40 sec. A considerable increase in retention with increasing basis weight is seen along with a broadening of the range over which the retention aid is effective. Similar results were found for the data at a contact time of 7.9 sec with all retention values being uniformly slightly lower. The maximum values of retention in Fig. 9 are shown plotted against basis weight in Fig. 10. The line is a linear least squares fit with a correlation coefficient of 0.99. The intercept at zero basis weight (54%) indicates the amount of retention occurring in the furnish before sheet formation commences. It does not differentiate between  $TiO_2$  adsorbed directly onto the fiber and that on pulp fines which are adsorbed onto the fiber before drainage. This value is considerably higher than those found by Williams and Swanson (6) using only simple electrolyte to mediate coflocculation. The difference is further quantitative indication of the improved retention to be obtained by using polymeric aids rather than relying on the reduction of colloidal repulsive forces by low molecular weight electrolytes.

The increase in retention above the intercept value in Fig. 10 accounts for the capture during drainage of  $TiO_2$  and fines and for mechanical sieving of large fines. It is seen that for the usual range of basis weights the proportion of retention attributable to these latter effects is considerable. The relative



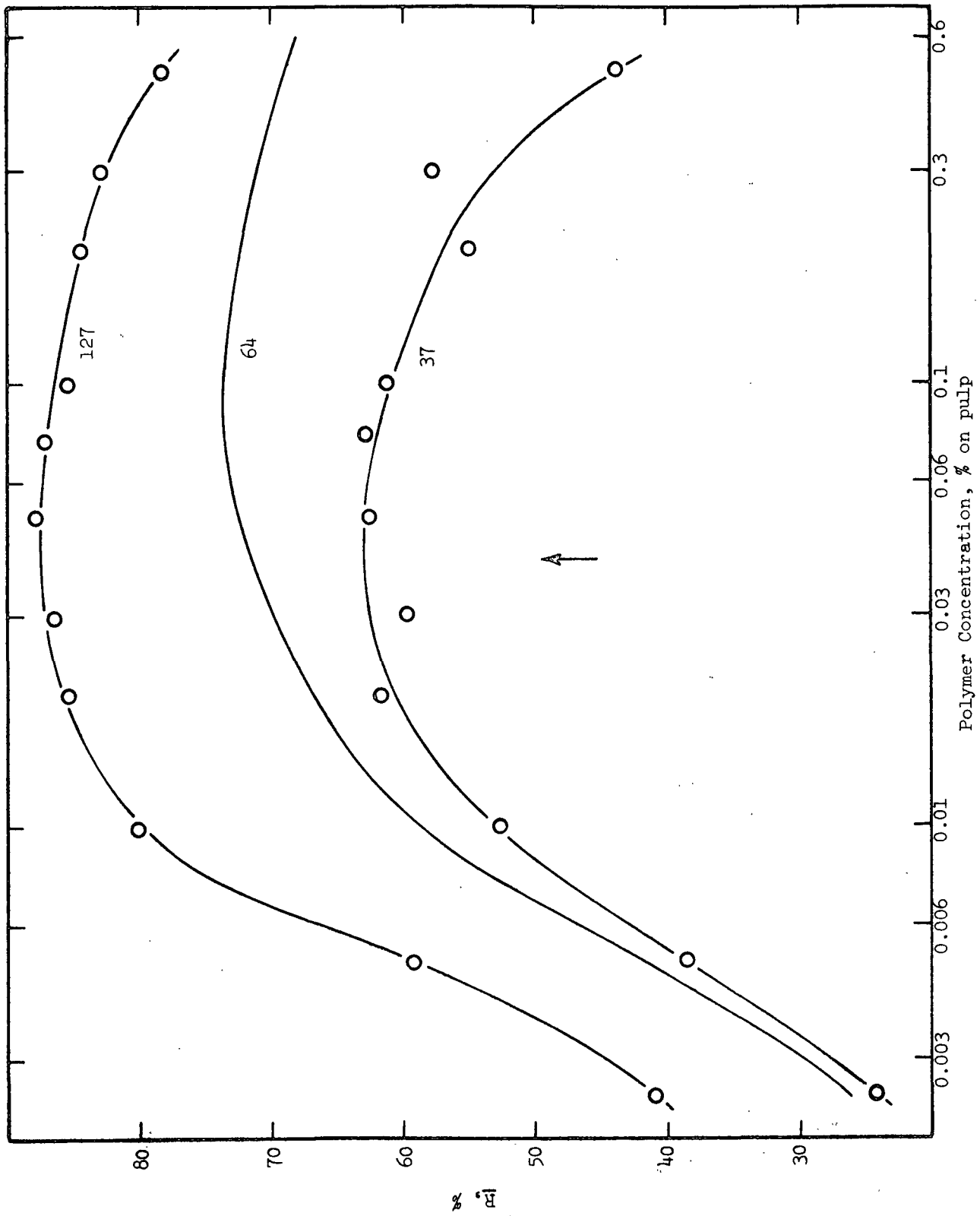


Figure 9. Effect of Basis Weight on Retention. Polymer: Q100. Pulp: No. 3 Whole. Numbers Indicate the Basis Weight in g/m<sup>2</sup>. Arrow Indicates Concentration at Zero Zeta Potential. Contact Time: 40 sec

proportions, as well as the absolute values, will depend upon the composition of the furnish and upon the particular retention aid used. This type of plot has been used previously (7) with handsheet data for the determination of "fines fraction" consisting of both pulp fines and filler.

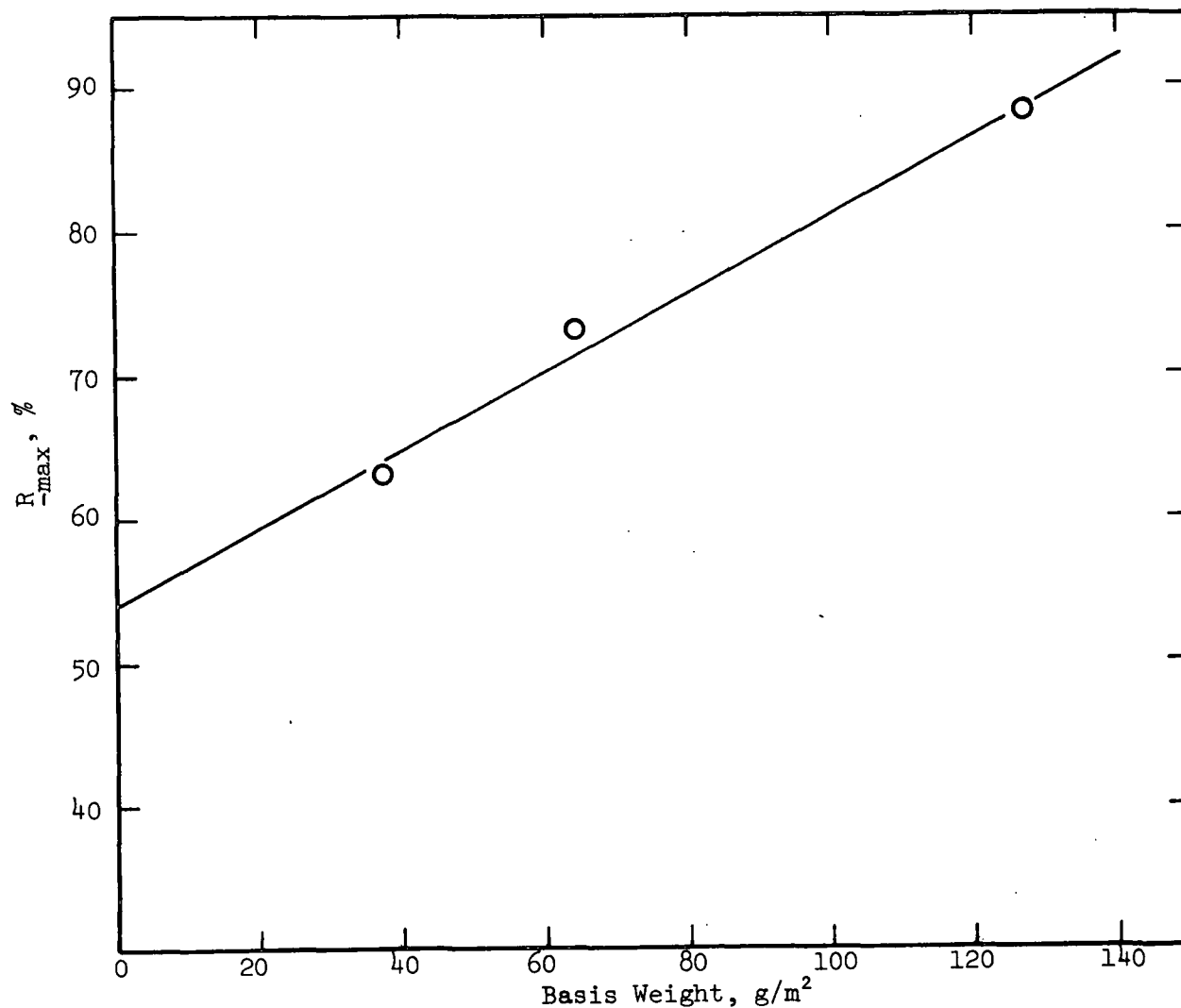


Figure 10. Variation of Maximum Retention with Basis Weight. Polymer: Q100. Pulp: No. 3 Whole. Contact Time: 40 sec

## EFFECT OF POLYMER DOSAGE

In Report One of this project the main thrust was the effect of contact time on the efficiency of the various polymers. For the most part only a single concentration (2 lb/ton) was used. In the present work we have limited the contact times to two and have emphasized the examination of the effect of polymer dosage on retention. A very broad span of polymer concentrations was employed — from the point where the effect of polymer addition is just beginning to appear (0.0025%) to that (0.5%) well beyond the economically feasible amount. The parameters of charge density and molecular weight of the retention aid were studied through the use of the polymers T100, Q100, and Q5.

Typical results are shown in Fig. 11 for whole pulp No. 3 at a contact time of 40 sec. The high-molecular weight polymers Q100 and Q5 exhibit good retention properties over a broad range of concentrations while the moderate molecular weight, high-charge density T100 is effective only over a narrow range. The trends in the curves of Fig. 11 may be used to explain why the retention with T100 reported previously (1) was so much poorer than that with Q100 or Q5. At a concentration of 0.1% T100 has already passed its peak while the other two are at their peaks. Note that the retentions with Q5 lag behind those of the other two aids at low concentrations. This is in line with the lower charge density of the polymer and suggests that electrostatic charge effects must be considered here.

The results for the same runs at a contact time of 7.9 sec are very similar in shape to those in Fig. 11 and will not be reproduced here. The values for retention are uniformly slightly lower than those for 40 sec.

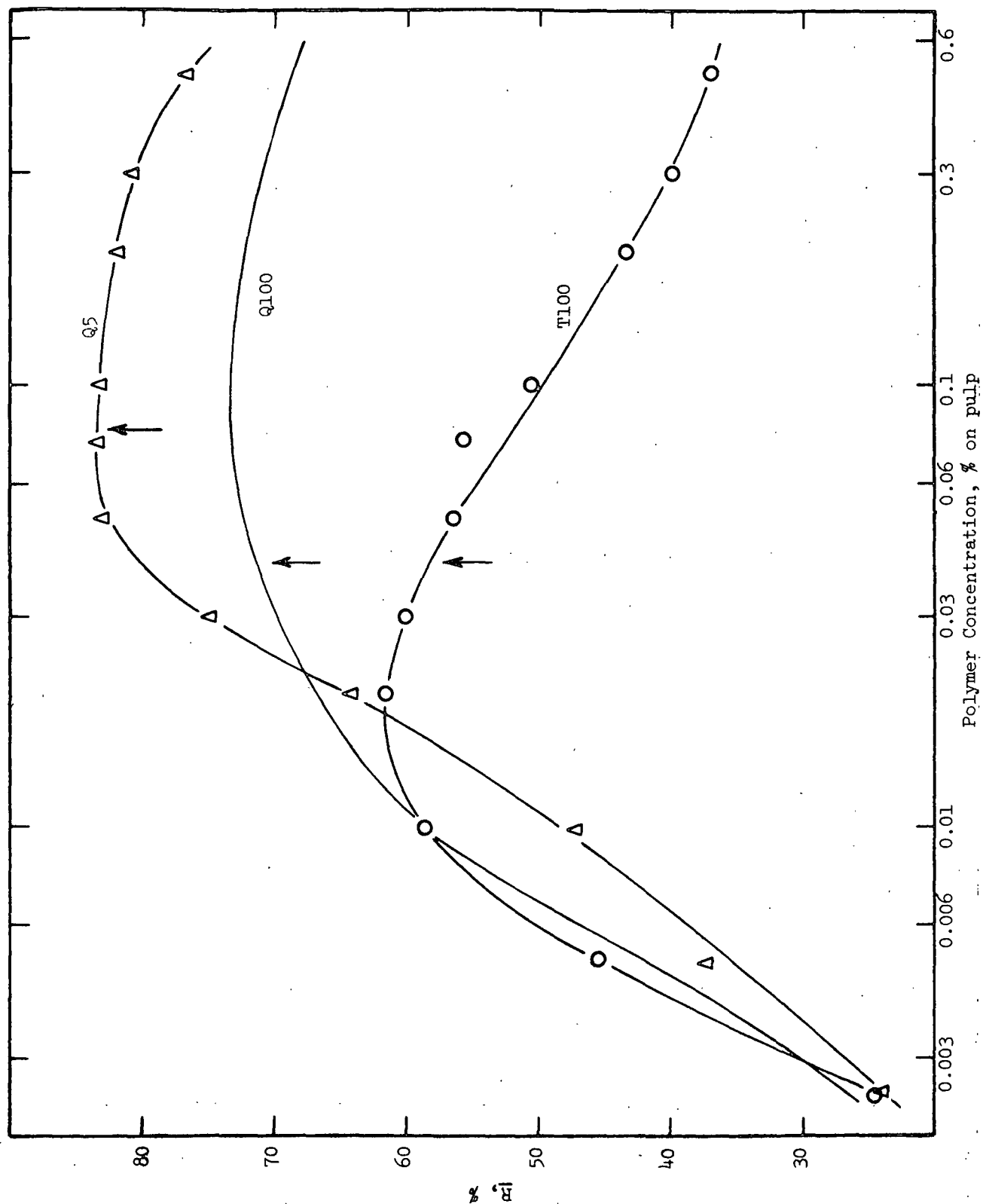


Figure 11. Variation of Retention with Polymer Concentration. Pulp: No. 3 Whole. Contact Time: 40 sec. Polymers: as Indicated. Arrows Indicate Concentrations at Zero Zeta Potential

Before proceeding with the interpretation of these data, we wish to examine first the effect of the same polymers on classified pulps. The results for classified pulp No. 3 at contact times of 40 and 7.9 sec are presented in Fig. 12 and 13, respectively. As with the whole pulp, polymer T100 produces its maximum effect at a very low concentration and then decreases monotonically at higher dosages. A salient feature here is the double maxima exhibited with polymer Q100 at both long and short contact times. (The individual data points for this polymer were shown in Fig. 2.) The other high-molecular weight polymer Q5 shows only a single broad maximum, and is clearly the most effective of the three. As in the case of the whole pulp the development of retention with increasing polymer dose for Q5 lags behind that for the other two polymers. We can again attribute this to the lower charge density of Q5. It is interesting that the maximum retention at 40 sec contact with T100 is equal to that of the much higher molecular weight material Q100.

Finally, the results of treatment of classified pulp No. 1 with T100 and Q100 at the two contact times are shown in Fig. 14. The behavior is similar to that for classified pulp No. 3. Polymer T100 yields a single maximum at low concentrations, while two maxima are found for Q100 at both contact times. The second maximum for Q100 at 7.9 sec is manifested as a shoulder on the low concentration side of the main peak. The retention values overall are rather low for this unbeaten, classified pulp, and it would be expected that they could be raised somewhat by longer contact times (cf. Fig. 5).

It now remains to provide an interpretation of the seemingly diverse behavior in Fig. 11-14. It is first to be noted that the maximum retention with T100 and the low concentration maximum (when it appears) for Q100 occur in the vicinity of zero zeta potential. This suggests that this maximum is due to

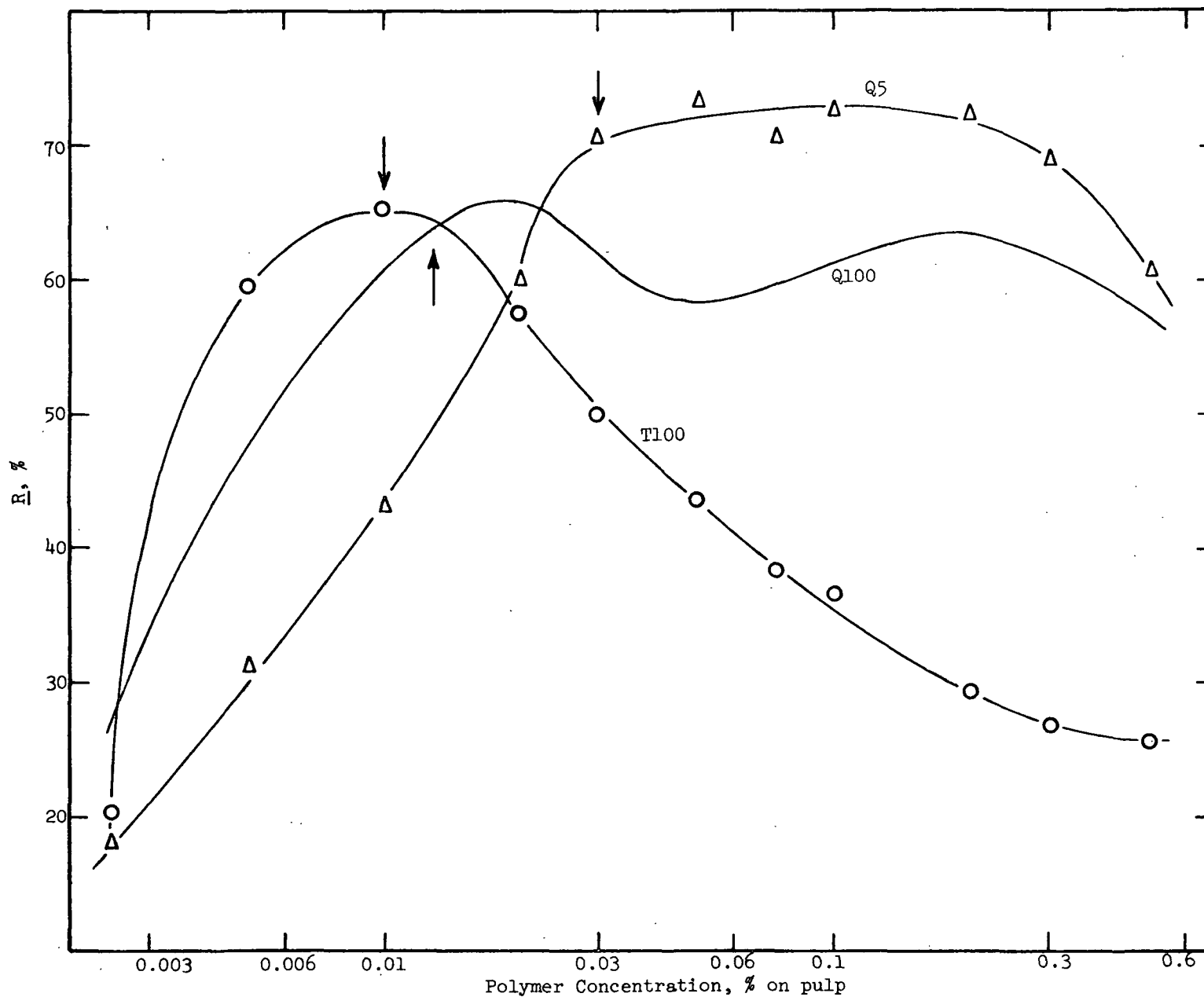


Figure 12. Variation of Retention with Polymer Concentration. Pulp: No. 3 Classified. Contact Time: 40 sec. Polymers: as Indicated. Arrows Indicate Concentrations at Zero Zeta Potential

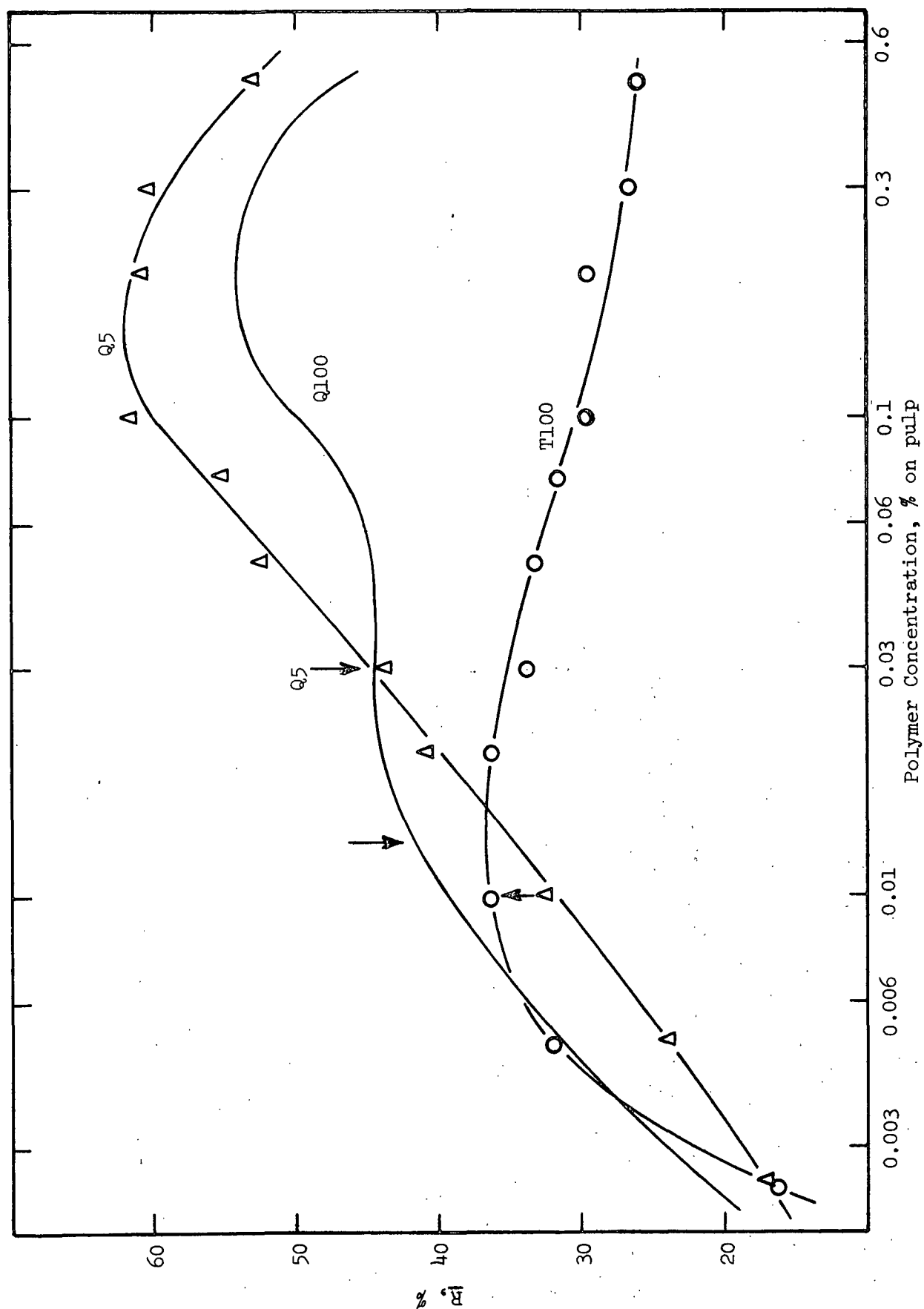


Figure 13. Variation of Retention with Polymer Concentration. Pulp: No. 3 Classified. Contact Time: 7.9 sec. Polymers: as Indicated. Arrows Indicate Concentrations at Zero Zeta Potential

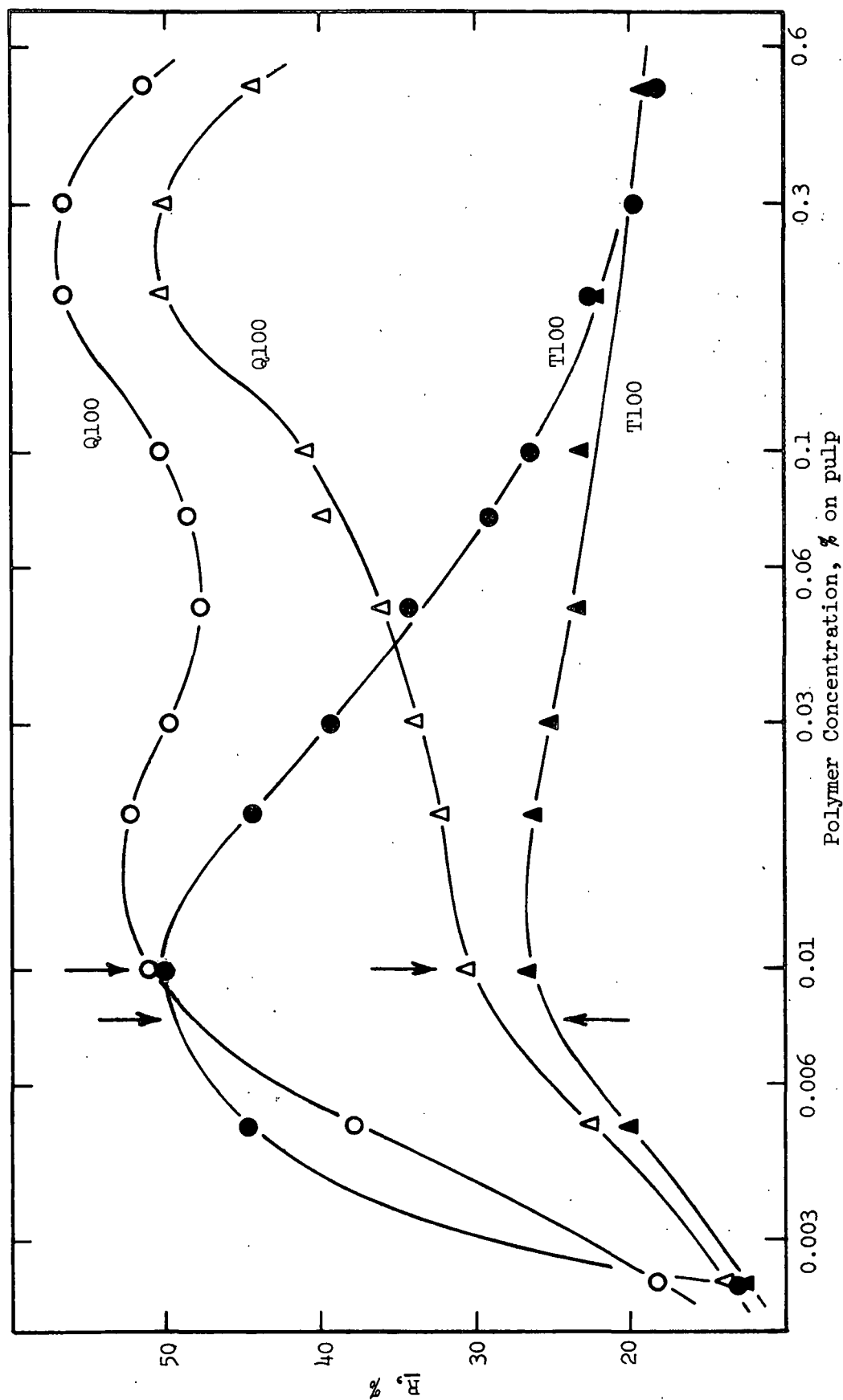


Figure 14. Variation of Retention with Polymer Concentration. Pulp No. 1 Classified. Polymers: as Indicated. Contact Times: Circles, 40 sec; Triangles, 7.9 sec. Arrows Indicate Concentrations at Zero Zeta Potential



charge neutralization of the various surfaces with concomitant coflocculation. Gregory (8) has recently shown that, when the mode of flocculation is charge neutralization, the equivalents of charge supplied by the flocculant to attain maximum effect is independent of molecular weight from simple cationic surfactant ( $M=364$ ) to high polymer ( $M=10^6$ ). Crude colloid titration determinations (9) indicate that the equivalents of charge per unit mass of T100 is about 1.5X that for Q100. This is in rough agreement with the positions of the peaks for these two polymers in Fig. 12-14. It also correlates with the polymer concentrations producing zero zeta potential although the latter may be dependent on molecular weight and chemical composition through the adsorbed polymer configuration.

Beyond the first maximum the zeta potential becomes increasingly positive with increasing polymer concentration. At 0.15% it is between +20 and +30 mv. for T100, Q100, and Q5 with classified pulps No. 1 and 3. For the moderate molecular weight T100 the strongly positively charged surfaces produce restabilization of the  $TiO_2$  and the retention drastically decreases. However, for high-molecular weight polymers Q100 and Q5 high levels of retention are found under the same electrokinetic conditions. The explanation would appear to lie in the concept of polymer "bridging" whereby a macromolecule can be simultaneously physically attached to two (or more) surfaces, thereby binding them together. It can be argued that the effects of bridging become apparent only at "high" concentrations because either 1) a certain threshold concentration must be reached before the probability of forming a bridge becomes sufficiently large or 2) a large zeta potential is necessary to facilitate extension of the polymer chain from the surface and make bridging more probable. Both these possibilities require that the cationic polymer "tail" adsorb onto a second surface that is

itself strongly cationic, at least as viewed by the macroscopic method of zeta potential determination. From a microscopic or "local" point of view there may be many negative or uncharged sites on the second surface that are favorable for cationic polymer adsorption. This is essentially the argument of "specific adsorption effects" that has traditionally been used (10) to explain the flocculation of negatively-charged particles by anionic polyelectrolytes. At the still higher concentration of 0.5% for Q100 and Q5 in Fig. 12-14 either the zeta potential has become prohibitively positive or the number of surface sites for secondary attachment has been reduced resulting in decreased retention.

The curves for Q100 in Fig. 12-14 provide information about the relative rates of the two processes, charge neutralization and bridging. The difference between bridging maxima at 7.9 and 40 sec contact time is about 6 and 9% for classified pulps No. 1 and 3, respectively. Thus, most of the retention has already occurred by 7.9 sec. On the other hand, the corresponding differences between the charge neutralization maxima at the two contact times is about 21% for both classified pulps indicating a much slower process. This is intuitively reasonable since the particles with extended polymer chains would be expected to have larger collision cross sections for retention than would the particles coflocculating by charge neutralization.

It is of interest that good retention is found also for the whole pulp (Fig. 11) at 0.25% for Q100 and Q5 where the zeta potential is again between 20 and 30 mv. The curious aspect is that approximately the same amount of polymer is required (say 0.25% of Q100) for good retention with both whole pulp No. 3 (Fig. 11) and classified pulp No. 1 although the hydrodynamic surface area of the former is 3X that of the latter. It must be concluded that the details of the bridging process, including effects of charge, are still only poorly understood.

The question can be raised that, if Q5 also mediates retention via charge neutralization and bridging, why are there not also two maxima for this polymer in Fig. 12 and 13? The answer is that, because of the lower charge density of this polymer, the two peaks are not sufficiently separated on the concentration scale to be visible. (Although two peaks could be found for Q5 in Fig. 12 by drawing the curve through all the points, the deviation of the data from the curve as drawn is within the standard deviation determined in an earlier section.)

A similar conclusion can be drawn for the results for Q5 and Q100 with the whole pulp (Fig. 11). Here the polymer concentrations for charge neutralization and for optimum bridging lie so close that only a single broad maximum is produced. It is likely that this is the case for most cationic, high-molecular weight polymers used as retention aids in the literature. It can be deduced that much of the confusion concerning the relative importance of charge neutralization and bridging for such materials derives from a blending of the two effects into the observed result. Also, the customary use of a linear rather than logarithmic scale for polymer dosage would tend to compress the two peaks, when they existed, into a single maximum.

Because the intrinsic viscosity of T100 with no electrolyte present is fairly large (1), it might be argued that some bridging was taking place with it, thereby vitiating much of the preceding argument. To check this, a run was made with P1, a low-molecular weight, highly-branched, compact macromolecule. Its hydrodynamic diameter is  $\leq 70$  A (11); it would not be expected to participate in bridging, as it is usually conceived, between the  $TiO_2$  particles ( $\sim 1500$  A in diameter). The resulting curve for whole pulp No. 3 is virtually identical in shape and magnitude with that for T100 in Fig. 11. It is concluded that T100 does not participate in bridging.

Although a retention maximum is seen to occur near the point of zero charge as measured by the zeta potential, this should not necessarily be interpreted as the same phenomenon as that resulting from specific (simple) ion adsorption. Indeed, the contiguity of the polymer segments suggests that on the "local" level there must be regions of the surfaces with high polymer segment density and others with effectively no polymer. It is only the net charge averaged over the entire particle that is measured by the zeta potential. Therefore, what has been called the charge neutralization mechanism in the preceding discussions is probably more closely akin to the electrostatic patch model of Kasper (12) and Gregory (13).

#### CONCLUSIONS

Effective polymeric retention aids derive their result in two ways.

1. They produce a large proportion of the retention of  $\text{TiO}_2$  to the fibers prior to sheet formation.
2. They effect good pulp fines retention during drainage.

Fibrillation increases retention in direct proportion to the hydrodynamic surface area produced. The increase is a result of the increased number of collisions/unit time of filler particles with fibrous material. The presence of pulp fines also increases retention by increasing the collision rate.

Both charge neutralization (or electrostatic patch mechanism) and polymer bridging play important roles in the ability of a high-molecular weight polymer to enhance retention. Moderate molecular weight retention aids do not participate in bridging. A strongly positive zeta potential caused by substantial polymer adsorption is necessary for bridging to occur. The development of filler retention via bridging is a much more rapid process than that due to charge neutralization.

## DRAINAGE STUDIES

## CONSTANT-RATE FILTRATION MEASUREMENTS

Effect of Polymer Structure on Drainage

The initial studies reported previously (1) have been extended to cover a wider range of drainage aids and polymer dosage rates. The filtration resistance data were analyzed in terms of the Kozeny-Carman equation (14) to give the hydrodynamic specific surface area  $S_{-w}$  and specific volume  $v$ . The same experimental procedures were used as before. Both Canadian Standard Freeness and constant-rate filtration measurements were run on the same batch of furnish.

The results for the various parameters for whole pulp No. 4 and a variety of polymers are listed in Table II. Included is the value for the filtration resistance,  $\bar{R}$ , at a pressure drop of 50 cm H<sub>2</sub>O. This pressure drop is in the mid-range of the experimental determination. Some of the data were reported earlier (1) but have been reproduced here for ease of comparison. It is evident that the polymers of moderate molecular weight and either low or high charge density (T5, P1, and T100) produce little change in the filtration resistance from that for the untreated pulp. Both the low-charge density (Q5) and high-charge density (Q100) high-molecular weight polymers produce decreased filtration resistance and decreased hydrodynamic specific surface area. Based on measurements on a large number of pulps in these laboratories, the precision in determination of  $S_{-w}$  and  $v$  is  $\pm 1\%$  and  $\pm 2\%$ , respectively (15). All the values for the specific volume fall within this range except those for Q100 at concentrations of 0.1 and 0.2%. Because these latter appeared to be outliers, measurements on duplicates of these furnishes were carried out on another day. Excellent reproducibility as seen in

Table II was found. Apparently, this polymer is capable of decreasing the specific volume. In view of the results for Q5, however, the major factor in the improvement of drainage would appear to be the decrease in surface area. Because drainage enhancement of classified pulps has been observed (1,16), it is of interest to enquire whether the decrease in surface area is associated with the pulp fines or the fibers. A series of experiments with classified pulp and classified pulp plus added fines was carried out to answer this question.

TABLE II

CONSTANT-RATE FILTRATION PARAMETERS FOR WHOLE PULP NO. 4

Polymer	Conc., % on pulp	$\frac{S_w}{w}$ , cm <sup>2</sup> /g	$\frac{v}{w}$ , cm <sup>3</sup> /g	CSF, ml	$\bar{R} \times 10^{-8}$ , cm/g ( $\Delta P = 50$ cm H <sub>2</sub> O)
None	--	35,200	2.90	195	13.6
T5	0.1	36,700	2.96	195	15.0
T5	0.2	35,500	2.88	195	13.8
T5	0.3	34,900	2.92	200	13.6
T5	0.5	34,800	2.91	220	13.4
T5	1.0	34,500	2.91	--	13.1
Q100	0.1	32,400	2.79	250	11.2
Q100	0.1	32,100	2.81	250	11.0
Q100	0.2	31,800	2.79	240	10.7
Q100	0.2	31,800	2.79	240	10.6
Q100	0.5	34,000	2.86	175	12.6
P1	0.1	34,500	2.87	245	13.0
T100	0.1	34,900	2.85	240	13.2
T100	0.2	35,000	2.87	200	13.4
Q5	0.1	34,000	2.86	255	12.5
Q5	0.2	31,400	2.86	280	10.6
Q5	0.3	27,500	2.89	290	8.24
Q5	0.4	28,300	2.91	270	8.79

#### Effect of Pulp Fines on Drainage

A series of furnishes was prepared by adding to classified pulp No. 4 calculated amounts of the white water produced during classification of pulp No. 4 to achieve fines levels of 5, 10, and 15% by weight of total pulp (fines plus

fibers). After thorough mixing at 0.5% consistency these furnishes were treated with either of two dosage levels of either Q5 or Q100. The levels were chosen as those that gave the maximum effect with the whole pulp discussed in the preceding section. Usually the polymer as a 0.1% solution was slowly added to the pulp with vigorous mixing. To check for uniformity of dosage to the pulp, two samples were treated using the Rapid Mixing Apparatus. Here the pulp at 1% consistency was mixed in the mixing tee with an equal volume of polymer solution of such concentration (very dilute) to give the desired add-on level. Thus, the final consistency was again 0.5%. The various samples were then subjected to constant-rate filtration measurements.

The results are presented in Table III and Fig. 15 and 16.

The first entries in Table III (with no added polymer) show that both  $\frac{S}{W}$  and  $\underline{v}$  increase with added fines. The nonconstancy of  $\underline{v}$  is in contradiction to previous work (17,18), which indicated that the fibers and fines at a given refining level possessed the same specific volume. It is possible that the irreversible drying during the classification process alluded to in an earlier section is responsible for the present results. Such drying would decrease the fiber surface fibrillation and would be equivalent to decreasing the degree of refining. Increased refining has been shown (17,18) to increase the specific volume. It should be pointed out that the conditions of the previous study (17) and those of the present were not identical. The pulps were bleached sulfite (17) and bleached kraft (present), and the refining was by ball milling (17) and by Valley beating (present). The possible effects of these differences are not known.

Other evidence suggests that a real difference between the specific volumes of fiber and fines exists. A plot of specific volume against percent fines

TABLE III

CONSTANT-RATE FILTRATION PARAMETERS FOR CLASSIFIED PULP NO. 4  
WITH VARIOUS LEVELS OF ADDED FINES

Polymer	Conc., % on pulp	Added Fines, % of total pulp	$\frac{S_w}{w}$ , cm <sup>2</sup> /g	$\frac{v}{w}$ , cm <sup>3</sup> /g	CSF, ml	$\bar{R} \times 10^{-8}$ , cm/g ( $\Delta P = 50$ cm H <sub>2</sub> O)
None	--	0	16,750	2.57	515	2.82
		5	26,300	2.74	345	7.29
		10	34,200	2.86	205	12.7
		15	43,000	2.95	135	20.7
Q100	0.1	0	15,200	2.58	550	2.32
		5	24,900	2.59	405	6.25
		10	32,900	2.80	260	11.5
		15	42,800	2.79	160	19.5
Q100	0.2	0	15,850	2.60	520	2.54
		5	23,900	2.62	405	5.84
		10	32,600	2.77	265	11.2
		15	41,800	2.79	165	18.4
Q5	0.1	0	15,000	2.62	575	2.29
		5	22,800	2.72	415	5.42
		10	32,200	2.82	260	11.1
		15	41,600	2.89	160	18.9
Q5	0.3	0	14,600	2.70	600	2.21
		5	21,100	2.84	455	4.81
		10	30,200	2.82	300	9.79
		15	38,000	2.85	180	16.2
Q5	0.1 <sup>a</sup>	5	20,500	2.78	505	4.43
Q5	0.1 <sup>a</sup>	15	41,200	2.90	230	18.6

<sup>a</sup>Polymer mixed with pulp in RMA.



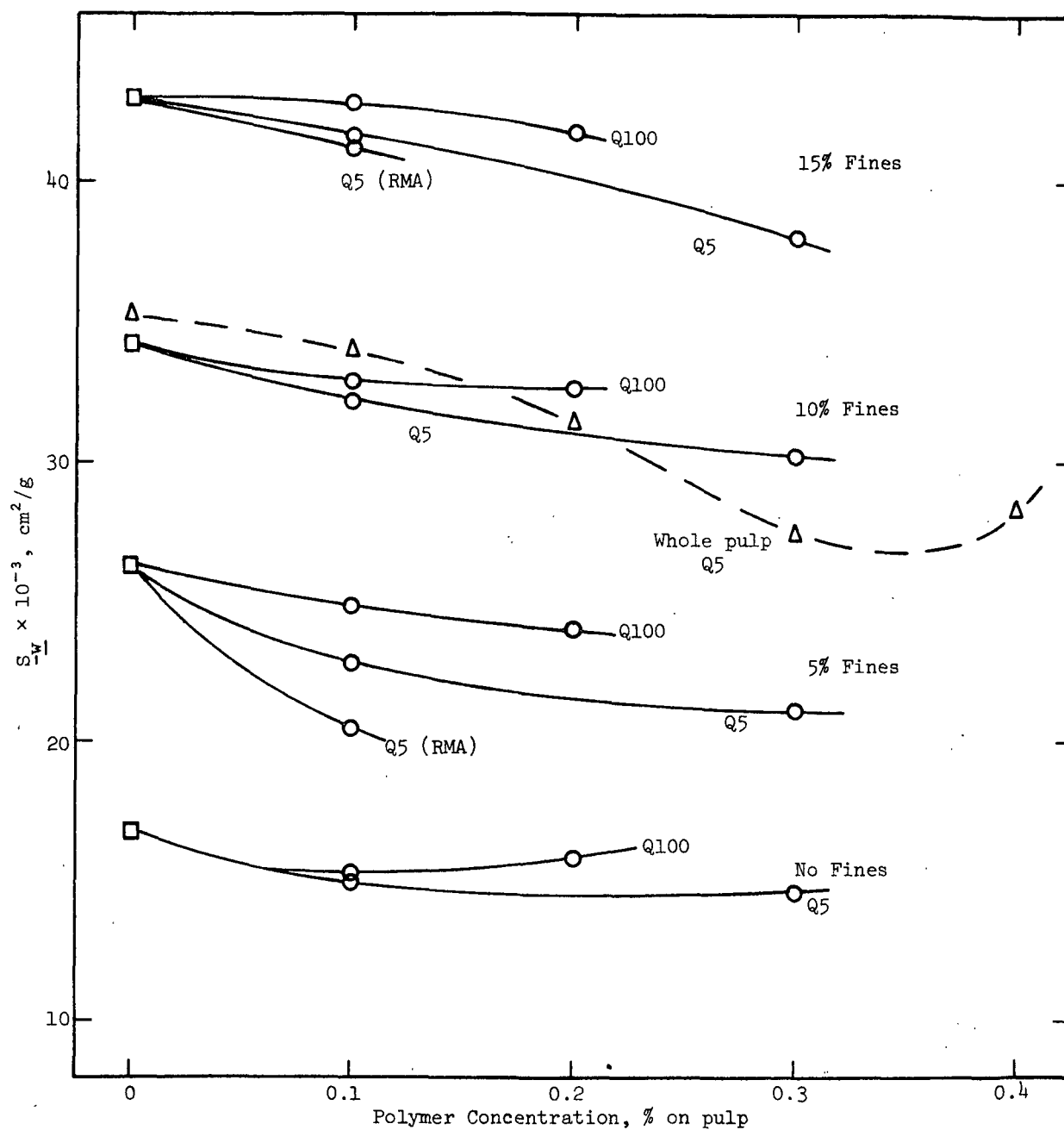


Figure 15. Dependence of Hydrodynamic Specific Surface Area on Drainage Aid and Fines Content

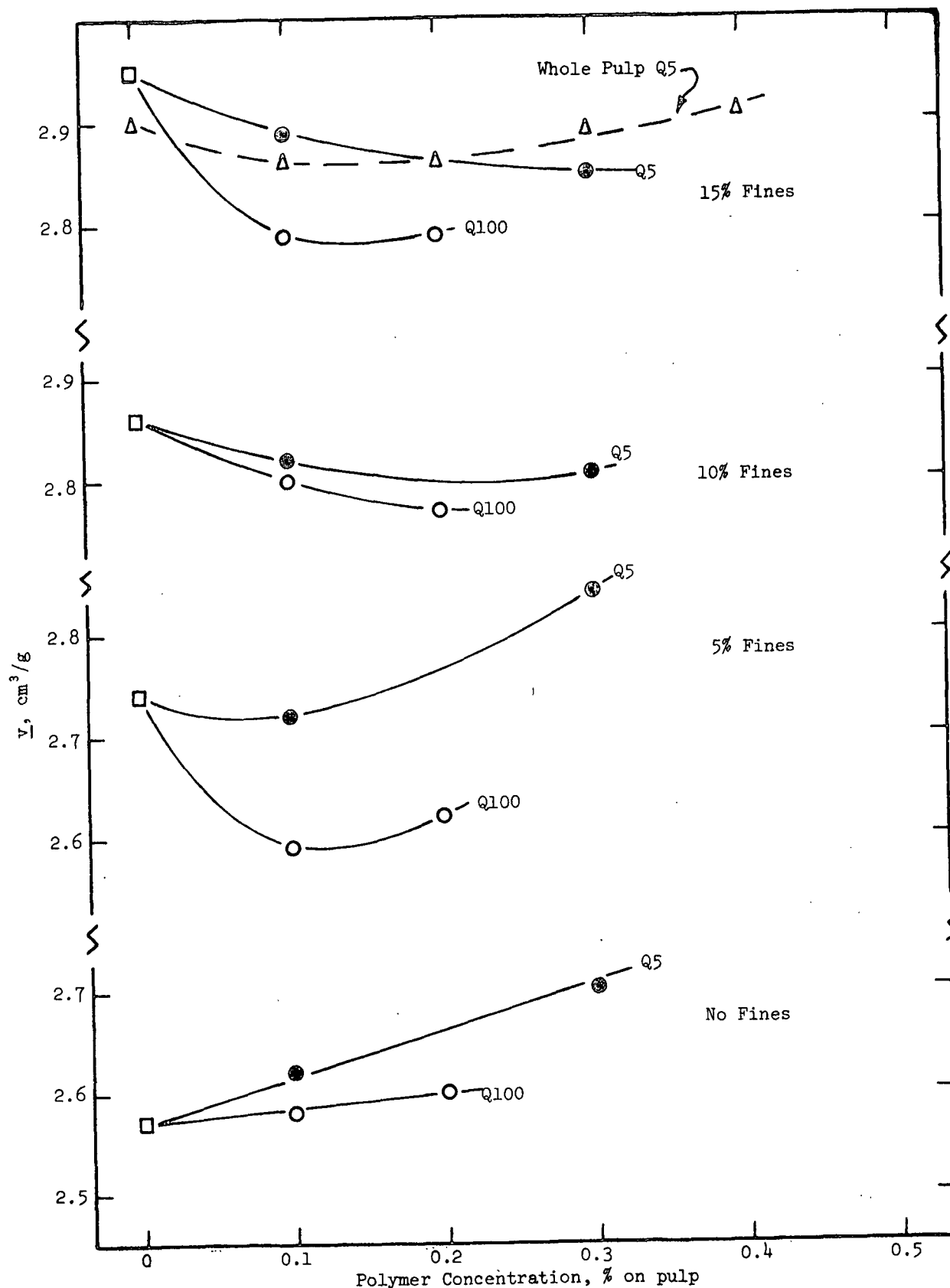


Figure 16. Dependence of Hydrodynamic Specific Volume on Drainage Aid and Fines Content

(with no polymer added) is linear. Least squares regression gives a correlation coefficient of 0.98. Assuming that the specific volumes of the fines and fibers are additive by weight fraction,

$$v = w_1 v_1 + w_2 v_2 \quad (2)$$

where

$\underline{v}$  = measured specific volume of furnish

$\underline{v}_1$  = specific volume of fibers

$\underline{v}_2$  = specific volume of fines

$\underline{w}_1, \underline{w}_2$  = weight fractions of fibers and fines, respectively

By interpreting the linear plot in terms of Equation (2), we can calculate specific volumes for the fibers and fines, and find values of 2.59 and 5.11 cm<sup>3</sup>/g, respectively. The latter value would appear to be much larger than might reasonably be expected for fibers beaten to this level of freeness. It must be concluded that either the fines possess a much larger specific volume than do the fibers or else the assumed additivity of volumes [Equation (2)] is incorrect. There is insufficient data available at present to further test the latter assumption.

The effect of drainage aids on the specific surface area is presented in Fig. 15. The following conclusions can be drawn:

1. Polymer Q5 is more effective at all levels of fines content in reducing  $\underline{S}_w$ . This behavior parallels that of the filtration resistance (cf. Table III).

2. The decrease in surface area with polymer treatment for all samples including the classified pulp indicates a change in the surface properties of the fibers. This may be a defibrillation (19) or dehydration of the microfibrils (20). In those systems containing fines, coflocculation of fibers and fines could also contribute to the decrease in surface area.

3. An overdose of polymer reverses the trend. This is most evident with no fines present (low surface area) but could presumably be found also for the other systems at still higher (uneconomical) dosages. Polymer Q100 reverses the trend at lower concentrations than Q5, suggesting that the effect is associated with the amount of charge on the polymer. The adverse effect of surface charge reversal due to polymer adsorption would produce less defibrillation than at the optimum dosage. The reduction in surface area is not just an effect of charge neutralization, however, since polymer Q5 is much more effective in reducing  $S_{-w}$  while affecting the surface charge less.

4. More efficient mixing of the polymer with the furnish produces enhanced surface area (and filtration resistance) reduction. The two samples labeled RMA in Fig. 15 were prepared in the RMA and represent near-ideal mixing conditions. The effect appears greatest at low levels of fines. These results emphasize again the importance of even distribution of polymer to the furnish to gain maximum efficiency.

5. Some irreversible drying took place during the classification process. This can be seen by the different shape of the curves for whole pulp (triangles) and for classified pulp plus fines. The surface area for the whole pulp with no polymer is in reasonable agreement with a fines content (through 150 mesh) of about 12% by Bauer-McNett classification. The large decrease in surface area with increasing polymer concentration suggests a greater fiber surface fibrillation for the whole pulp compared to that of the classified pulp. The importance of mechanisms of drainage aid action other than that of fines co-flocculation is evident.

The data in Fig. 15 can be cross-plotted as specific surface area against percentage fines at constant conditions of polymer addition. The resulting curves

are linear as might be expected upon the assumption of additivity by weight fraction in Equation (3).

$$S_{\underline{w}} = w_1 S_{\underline{w},1} + w_2 S_{\underline{w},2} \quad (3)$$

Here

$S_{\underline{w}}$  = measured specific surface area

$S_{\underline{w},1}$  = specific surface area of the fibers

$S_{\underline{w},2}$  = specific surface area of the fines

$w_1, w_2$  = weight fractions of fibers and fines, respectively

The results of linear regression analysis of the plots and the parameters derived using Equation (3) are listed in Table IV.

TABLE IV

HYDRODYNAMIC SPECIFIC SURFACE AREAS OF FIBERS AND FINES

Polymer	Conc., % on pulp	$S_{\underline{w},1}$ (Fibers), cm <sup>2</sup> /g	$S_{\underline{w},2}$ (Fines), cm <sup>2</sup> /g	$r^2$ <sup>a</sup>
None	--	17,100	190,000	0.999
Q100	0.1	15,300	197,000	0.998
Q100	0.2	15,500	188,000	0.999
Q5	0.1	14,500	192,000	0.998
Q5	0.3	14,100	173,000	0.996

<sup>a</sup>Correlation coefficient of plot of  $S_{\underline{w}}$  vs. % fines.

The calculated values of  $S_{\underline{w},1}$  are in good agreement with the values for  $S_{\underline{w}}$  obtained on the classified pulp and verify that the drainage aids do decrease the specific surface area of the fibers. The effect of the polymers on  $S_{\underline{w},2}$  is not certain. Although the correlation coefficients appear excellent, visual examination of the plots reveals some scatter of the data about the lines. Thus,

within the experimental error it is not possible to conclude that the polymers have produced a change in the specific surface area of the fines. The changes, if present, are certainly much smaller on a relative basis than those found for the fibers. (On an absolute basis the maximum change found for the fibers,  $3000 \text{ cm}^2/\text{g}$ , is within the experimental error of the values for  $S_{-w,2}$ .) These results suggest that it is the effect of the polymer on the fiber rather than on the fines that is the controlling factor in drainage enhancement.

From the values of  $S_{-w,1}$  and  $S_{-w,2}$  in Table IV of the untreated stock, the relative contributions of the fiber and fines to the total surface area can be calculated using Equation (3). For 5, 10, and 15% fines the fractional area (on a percentage basis) attributed to the fines is 37, 55, and 66%, respectively. The analogous calculation can be made for the specific volume using the values quoted earlier ( $2.59$  and  $5.11 \text{ cm}^3/\text{g}$  for fibers and fines, respectively). We find at fines levels of 5, 10, and 15% that the fines contribute 10, 18, and 26% to the total specific volume. Thus, the fines influence the specific surface area to a much greater extent than they do the specific volume.

The effect of drainage aids on the specific volume is much smaller than the effect on the surface area, as can be seen in Fig. 16. (Note the broken ordinate to provide clearer identification of the several curves.) The conclusions to be drawn on the basis of this figure are, therefore, not nearly so strong as those concerning the specific area. Indeed, upon considering the experimental precision, one doubts that any meaningful comments could be made about any single curve without many replications of the experiments. However, taken as a whole, the data appear to display a number of definite trends whose discussion may be illuminating:

1. Both drainage aids appear to increase the specific volume of the fibers (no fines case) in direct proportion to their dosage. The reconciliation of this interpretation with the corresponding decrease in specific area (same samples) may be difficult.

2. For furnishes with added fines two factors appear to be at work, tending to decrease the overall specific volume at low polymer dosages and to have the reverse effect at higher dosages. From the shapes and positions of the several curves it can be argued that the polymers decrease the specific volume of the fines. Only at higher dosages does the effect on the fibers (increase in specific volume) occur, since much of the polymer is adsorbed by the fines. In agreement with this interpretation, the minimum in the curves shifts to higher polymer concentrations with increasing fines content.

3. The small change in the values for the whole pulp, together with a minimum at a fairly low polymer dosage, suggests that the surface fibrillation is greater for this sample. That is, the fiber surface of the whole pulp is able to adsorb a greater proportion of the polymer at a given dosage than is the classified pulp to which a similar amount of fines have been added. This interpretation is in line with other evidence above of the reduced fibrillation of the classified pulp.

4. Polymer Q5 is more effective than Q100 in increasing the specific volume of the fiber surfaces (no fines case). Continuing the interpretation offered in point 2 above, we conclude that Q100 is more effective than Q5 in decreasing the specific volume of the fines.

It must be reiterated that the points made above are somewhat speculative. They involve interpretations which rely on the assumption of minimum error in the data of Fig. 16. As mentioned previously, it is only by considering the

whole mass of data together, that it is felt that the points made have some validity.

It has been tacitly assumed throughout this discussion that the compressibility of the furnishes was constant. Measurements of the compressibility were not made for all samples but only for a few representative of the largest deviations in filtration resistance from the untreated whole pulp. The compressibility was found to be independent of classification, % added fines, and polymer treatment verifying the assumption of its constancy.

On the basis of Fig. 15 and 16, it can be asked which parameter,  $S_w$  or  $v$ , can be modified to enhance the drainage properties of a pulp? Polymer Q5 provides the greater decrease in filtration resistance (and increase in freeness) and the greater changes in specific surface area. On the other hand, Q100 provides greater decreases in specific volume for pulps containing fines, while being less effective than Q5 in decreasing filtration resistance. From these observations it follows that decreases in specific surface area caused by polymer treatment correlate more closely with decreased filtration resistance than do changes in specific volume or (nonexistent) changes in compressibility.

It can be speculated that it is the enhanced ability to form bridges due to its high molecular weight and low charge density that allows Q5 to perform better as a drainage aid than Q100 or the other polymers in Table II. It is this same bridging ability that was used to explain this polymer's excellent  $TiO_2$  and fines retention in the previous section. Evidently, this property can provide increases in both drainage and retention.

Although constant rate filtration measurements permit interpretation in terms of hydrodynamic specific surface and specific volume, it is often more



expedient to carry out a simple freeness measurement. It is important, then, to know whether a good correlation exists between filtration resistance and freeness. Other work (17,21) suggests a reverse sigmoidal curve when Schopper-Riegler freeness is plotted against the logarithm of filtration resistance. For the present experiments Canadian standard freeness was measured on the same samples as the filtration resistance. The results from Tables II and III are plotted in Fig. 17. A linear correlation (on this semilogarithmic plot) is found over the whole range of freenesses examined. All samples, whole and classified pulps, pulps with added fines, and pulps treated with polymers or untreated are presented. Linear least squares regression analysis gave the equation

$$\text{CSF} = 4337 - 451.4 \log \bar{R} \quad (4)$$

with a correlation coefficient  $r^2$  of 0.981. The data points shown as closed circles are those from the samples prepared by mixing in the RMA and do not appear to fit this correlation. They were not included in the regression analysis. This is further evidence that these samples, prepared to ensure maximum uniformity of polymer treatment, are quantitatively "different" from the other samples. For comparison with the previous work (17,21) the range of Schopper-Riegler freeness values covered in Fig. 17 corresponds approximately to 385-835 ml SR. Because the correlation between Schopper-Riegler and Canadian standard freenesses is non-linear, it is not surprising that their respective correlations with filtration resistance would exhibit different shapes. It is expected that the linear relationship found in Fig. 17 may not hold at very low or very high levels of freeness.

The filtration resistance at the arbitrarily chosen pressure drop of 50 cm H<sub>2</sub>O was used in the correlation, but it is suspected that equally good correlations could be obtained at other pressure drops. The salient point is

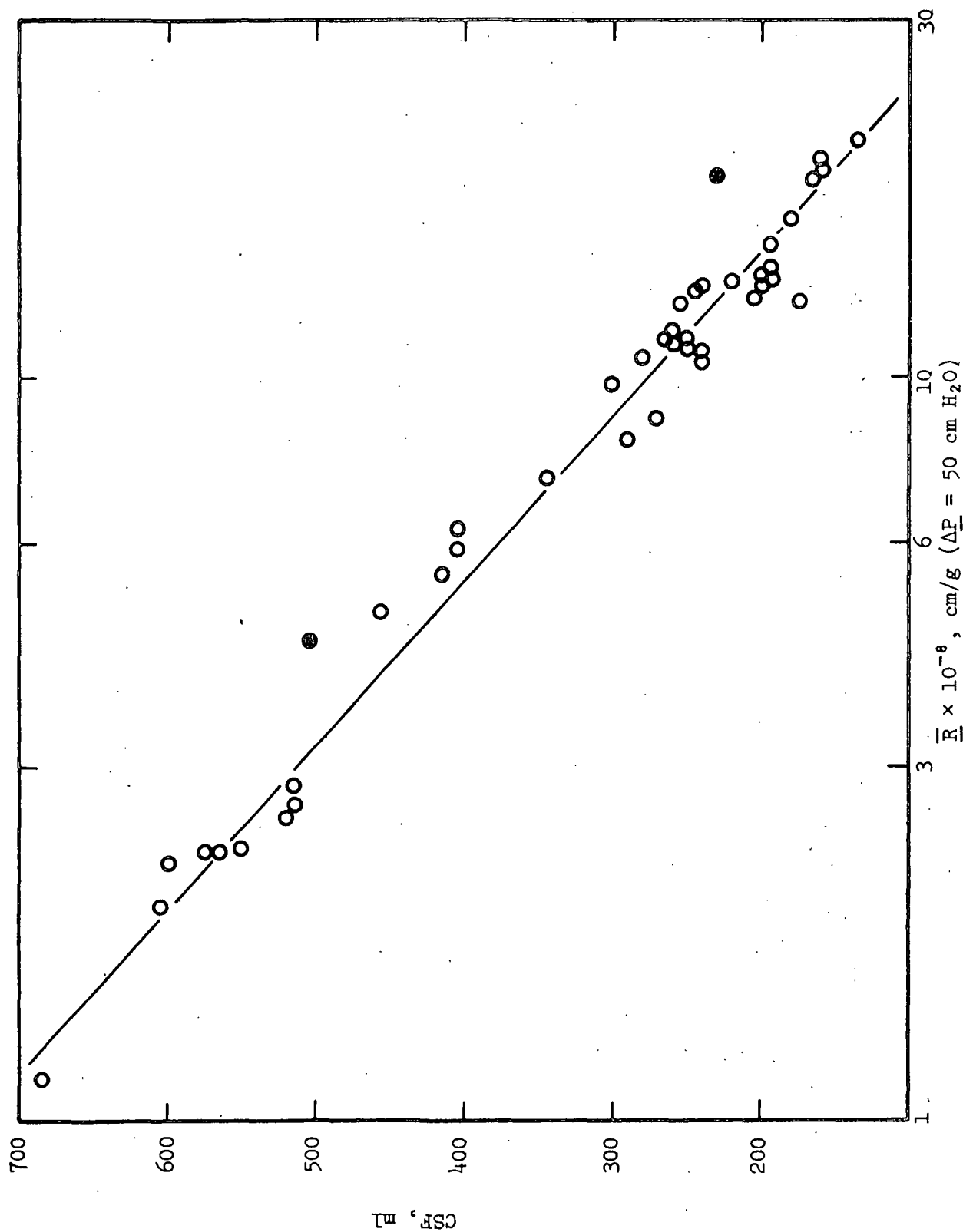


Figure 17. Variation of Canadian Standard Freeness with Filtration Resistance for the Furnishes in Tables II and III

that the Canadian standard freeness is a valid measure of a pulp's drainage properties when a detailed analysis of the hydrodynamic parameters is not desired.

#### EFFECT OF DRAINAGE AIDS ON WET PRESSING

It has often been claimed that drainage aids, in addition to enhancing drainage on the wire, also improve water removal in the presses. But few hard data are available in the literature. Poschmann (22) studied the application of polyethylenimine to a waste fiber furnish used to produce a heavy grade of chip board. By measuring the percentage solids at various points on the paper machine, both with and without the drainage aid, he was able to show improvement in dewatering both on the wire and in the presses.

The present study was designed to gain information on the amount of additional dewatering that could be possible during wet pressing if drainage aids were used. The goal was to simulate actual machine conditions in so far as the available equipment allowed.

#### Experimental

The experiments were comprised of two parts: sheet formation through couching and sheet pressing. In order to economize on materials and expense, a batch rather than continuous system was run. Standard 2.5 g sheets ( $58.6 \text{ g/m}^2$  basis weight) were formed in an 8 × 8 inch Noble & Wood sheet mold. The stock was No. 4 whole pulp and was adjusted to pH 5 with  $\text{H}_2\text{SO}_4$ . When polymer was used, it was added as a 0.1% solution to the pulp (0.5% consistency) with rapid stirring for 5 minutes. The sheet was formed as usual from a 0.04% consistency slurry on a 100-mesh Monel wire in the sheet mold.

The sheet was couched from the wire by placing two 9 × 9-inch blotters on the wet sheet and passing a solid brass Noble & Wood couch roll over the wet sheet/blotter stock for a total of six passes. The couched sheet was then transferred to a 10 × 12 × 0.0029-inch mylar film by couching with a very light roll. The couched sheet/mylar film sandwich was then placed in a tared polyethylene bag which was then closed and weighed. (The mylar film acted as a backing and allowed the several subsequent manipulations of the fragile sheet.) This method produced sheets of approximately constant o.d. weight (average = 2.51 g, standard deviation = 0.06 g) and constant moisture content: average = 25.17% solids, standard deviation = 0.41% solids. This moisture level would be typical of the web coming off the couch roll or off the first press depending on the particular paper machine and grade. Some experiments (not reported here) were also done using less pressing during couching to give sheets of about 16% solids. The precision on these experiments was less although the trends were the same as those to be described below.

The second part of the experiment concerned the simulation of the wet pressing operation. This was carried out using the press section of the IPC High Speed Wet End operating at 150 fpm. This is composed of a single nip with a felt passing between two smooth 16-inch-diameter steel rolls. To maintain better control over the felt moisture content, a small (10 × 15 inches) felt swatch was arranged in a sandwich with the couched sheet/mylar film. A schematic is shown in Fig. 18. Ten of these felt swatches had been cut from a single top pickup felt (75% wool/25% synthetic) to ensure uniformity. They were preconditioned by soaking overnight in deionized water, then by passing twice through the nip of the High Speed Wet End press at a pressure of 400 pli, and then were stored in closed polyethylene bags until used. Before the felt swatches were pressed, the continuous felt of the press section was also conditioned by being sprayed with water and then pressed in the nip at 400 pli.

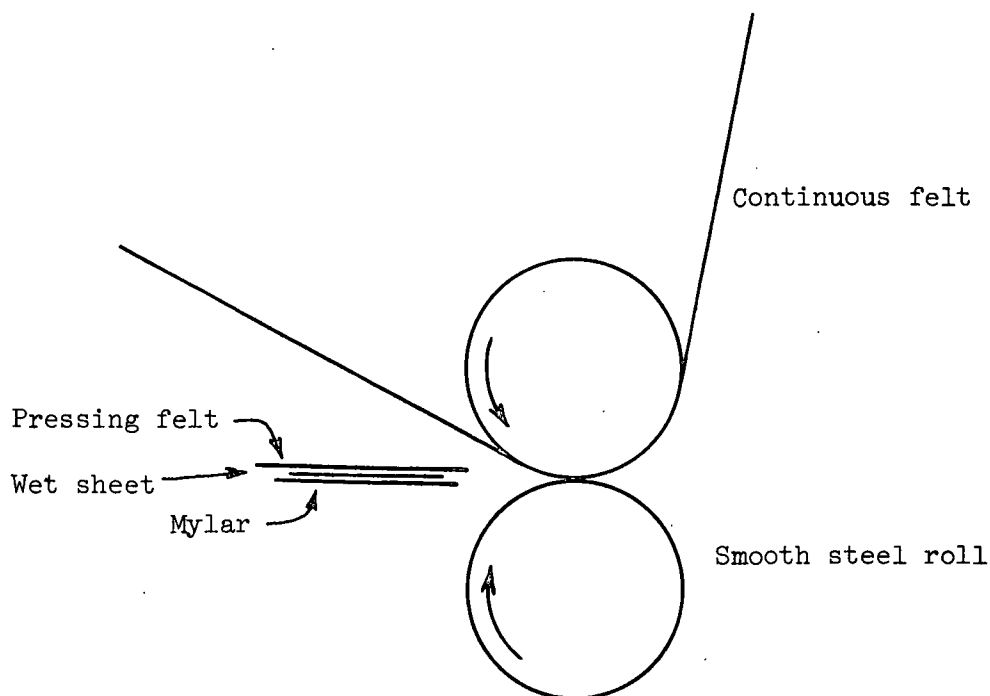


Figure 18. Schematic of Wet Pressing Experiment

When the felt swatch conditioning was completed, a felt swatch was removed from the bag, a couched sheet/mylar film composite was removed from its bag, and a triple-decker sandwich was assembled. This sandwich was then passed through the nip as shown in Fig. 18, the felt swatch was removed, and the pressed sheet/mylar film composite was returned to its bag. The exposure time of the couched or pressed sheet to the atmosphere was minimized to prevent extraneous moisture transfer. Since the mylar is nonabsorbent, all the water pressed from the sheet is transferred to the felt swatch. Two pressures were utilized for the wet pressing: 110 and 220 pli. Attempts to use still higher pressures resulted in "crushing" of the paper.

The pressed sheet/mylar film sandwich in its polyethylene bag was then reweighed. Finally, the pressed sheet was removed, dried overnight at 105°C, and reweighed. From these several weighings (to  $\pm 0.01$  g) the solids content

of the sheet before and after pressing could be calculated. The percentage solids after pressing varied from 30-33% at 110 pli and 34-38% at 220 pli.

### Results and Discussion

The increase in solids due to the pressing operation for the various samples is listed in Table V. In addition to control runs (no added polymer), three different drainage aids were tested. The dosage levels for these were chosen as those which had produced the maximum decrease in filtration resistance in the experiments discussed in the previous section. Samples were run in quadruplicate at each of the polymer treatments and at each of the two pressure levels. The four results at each condition were averaged and the standard deviation was calculated.

From the results in Table V it is immediately apparent that (a) the effect of the drainage aids is small, and (b) the precision of these experiments is poor. When the size of the sample is considered, the reason for the latter becomes evident. A change of 1% in solids at the 30-35% solids level corresponds to a weight change of only 0.29-0.20 g. It appears likely that variations of this magnitude could occur during the pressing and handling operations.

As a result of the poor precision the data were subjected to a statistical test for significance. The hypothesis tested was that the average increase in solids with a polymer additive was equal to the average value for the corresponding control. Utilizing the Student's  $t$  test, we find that the hypothesis can be rejected at the 90% confidence level for the samples with 0.2% P1 and 0.1% Q100 at a pressure of 110 pli. For these samples then, the drainage aids provide a definite gain of about 1% in solids over the control. For the 0.3% Q5 at 110 pli and all the samples at 220 pli, the small difference in means between

the treated and control samples and the relatively large standard deviations combine to disallow the rejection of the hypothesis at the 90% confidence level.

TABLE V

## DEWATERING IN WET PRESSING USING VARIOUS DRAINAGE AIDS

	Increase in Solids, percentage points			
	Control	0.2% P1	0.1% Q100	0.3% Q5
Pressure: 110 pli				
	7.54	7.66	7.93	5.53
	5.88	7.67	7.81	6.17
	6.10	7.59	8.02	6.42
	6.89	8.05	6.86	5.98
Average	6.60	7.74	7.66	6.03
Std. dev.	0.76	0.21	0.54	0.38
Pressure: 220 pli				
	9.78	10.95	10.17	9.76
	8.55	9.51	10.99	9.08
	10.10	9.56	10.71	8.82
	11.03	12.69	9.80	9.37
Average	9.87	10.68	10.42	9.26
Std. dev.	1.02	1.50	0.53	0.40

Subjectively, we can say that the treatment with Q5 at 110 pli appears to provide a decrease in solids when compared with the control. Similarly, at a reduced confidence level, we can argue that the trends noted at 110 pli for the various samples appear to hold also at 220 pli.

The fact that treatment with 0.3% Q5 gave no effect (at the 90% confidence level) is surprising since the corresponding results for filtration resistance indicated this polymer reduced  $\bar{R}$  twice as much as did the treatments with P1 and Q100. This finding suggests that the drainage aid providing the driest sheet off the couch may not provide optimum benefits in the press section. Alternatively, it may be advantageous on a particular machine to choose a polymer which provides some (less than maximum) benefits both on the wire and in the presses. More work is necessary to prove that differences in drainage aid performance can occur on the wire compared with the presses and, if proved, to elucidate the different mechanisms responsible.

#### MEASUREMENT OF DRAINAGE TIMES ON THE RAPID MIXING APPARATUS

A great deal of information has been obtained with the Rapid Mixing Apparatus on the effect of contact time and polymer dosage on filler and fines retention. It was suggested that the utility of the instrument could be increased by a simple modification to permit a concurrent measurement of the drainage rate (23). It has also been found (24) that laboratory measurements of drainage under vacuum provide better correlation with paper machine results than do those from standard freeness tests. A description of the modification and some preliminary results are presented below.

#### Experimental

The technique involves measuring the average drainage rate of the stock in the deckle box during sheet formation when using the RMA in the sheet mold mode. This was accomplished by placing two electrodes in a vertical plane in the wall of the deckle box opposite the inlet from the mixing tee. They were 1.00 cm apart. A third electrode contacting the septum wire served as a ground.



The distance from the wire to the lower electrode was 0.85 cm. A schematic is shown in Fig. 19. An electronic interface between the electrodes and an electronic timer (Precision digital timer, model STD-11-2, Standard Electric Time, Springfield, MA) starts the timer when the draining furnish reaches the upper electrode and stops the timer when the furnish reaches the lower electrode. The electronic interface consists of an "exclusive OR" integrated circuit controlling a transistor which triggers the timer. The system is extremely sensitive so that even distilled water provides sufficient conductance between the electrodes for satisfactory operation. The timer measures the elapsed time to the nearest millisecond. The stainless steel wire electrodes were encased (except for their tips) in coaxial cylinders of Teflon which were then polished to present smooth, hydrophobic surfaces to the furnish. The objective here was to minimize the adhesion of water drops or fiber during drainage. Such adhesion, when it occurred on the upper electrode, led to spuriously short drainage times with the opposite result on the lower electrode. Indeed, this phenomenon has proved to be the only non-negligible source of error in the precision of the measurements. It is possible that a modified electrode design could further reduce this error.

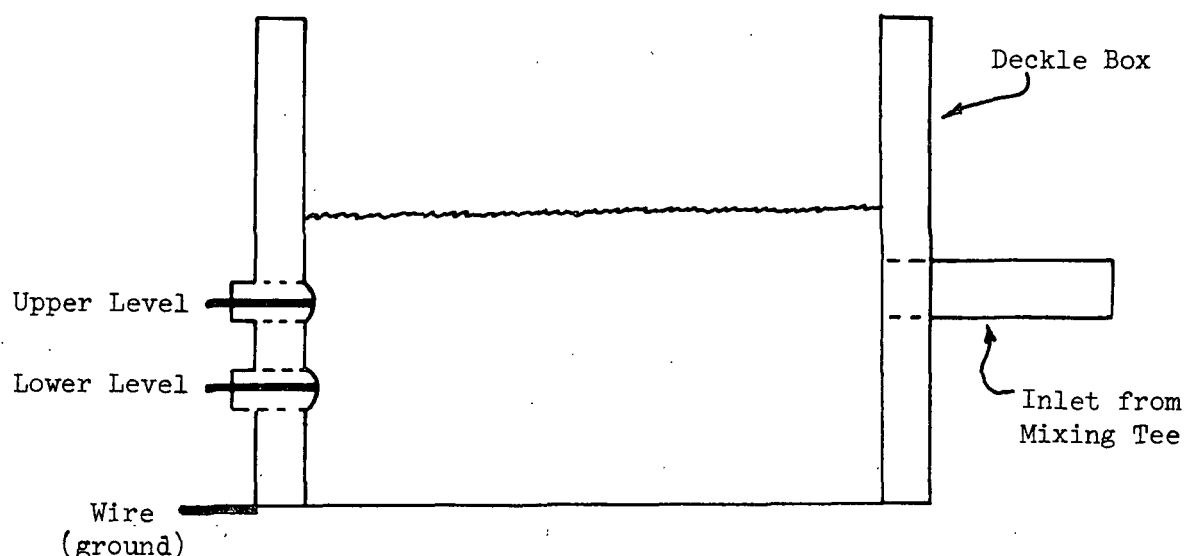


Figure 19. Schematic of Drainage Rate Modification of RMA  
(Cross-sectional View)

The operation of the instrument was tested using distilled water as the draining fluid. A series of replicates yielded an average value for the drainage time of 7 msec with a standard deviation of 1 msec. Because the electrodes are 1 cm apart, the reciprocal of the drainage time (in sec) gives the average drainage rate. For water this is 143 cm/sec which represents the maximum drainage rate possible at the applied vacuum (10-inch Hg). Evidently, the instrument is capable of precise measurements at very short times.

### Results and Discussion

Several runs were carried out at the usual basis weight for sheet mold mode operation, 67.5 g/m<sup>2</sup>. The surprising feature was that little, if any, decrease in drainage time was observed upon treating a furnish with a known drainage aid (e.g., Q100 or Q5). Upon reflection a reason for this behavior became apparent. The thickness of the pad changes continuously during drainage. When sheets of moderate basis weight are formed, only a very thin pad is present during most of the timed flow. Since the resulting pressure drop across the pad is low, the sheet has a very open structure and little resistance to flow. Hence, drainage aids might be expected to have little effect on the drainage rates as, indeed, was noted above. Analogous to this behavior is the observation (24) that drainage aids have no influence on drainage on a fourdrinier during the early stages of sheet formation where high porosity permits relatively unimpeded flow.

To test the explanation given above, we formed series of sheets at different basis weights. Whole pulp No. 3, either treated with 0.3% Q5 or untreated, was the furnish. The contact time was kept constant at 7.9 sec. By varying the amount of 0.25% consistency furnish admitted to the deckle box, we could prepare sheets of differing basis weight. Since the electrode positions are fixed, the

drainage time for flow through pads of different thickness was being measured as the basis weight was varied.

The results are listed in Table VI. The average basis weight  $\bar{w}$  is defined as the basis weight of the pad when the furnish level has dropped to the midpoint between the upper and lower electrodes. (This quantity can be simply calculated from the dimensions of the apparatus and the initial height of the furnish in the deckle box.) The final basis weight  $w_f$  of the drained sheet, the average drainage time and its standard deviation,  $\sigma$ , are also given. As noted previously the drainage aid has little effect on the lightest sheet. The improvement in drainage afforded by use of the polymer at increasing basis weights is readily apparent. It is believed that the variance in the values at a given condition is due to the problem of the furnish not breaking cleanly with the electrodes.

TABLE VI  
EFFECT OF BASIS WEIGHT ON DRAINAGE AID PERFORMANCE

(Whole Pulp No. 3)

$\bar{w}$ , g/m <sup>2</sup>	$w_f$ , g/m <sup>2</sup>	Drainage Time, sec			
		Control		0.3% Q5	
		Average <sup>a</sup>	$\sigma$	Average <sup>a</sup>	$\sigma$
33.7	67.5	0.061	0.007	0.058	0.004
68.7	102.5	0.200	0.013	0.176	0.008
92.5	126.2	0.331	0.021	0.226	0.020
113.7	147.5	0.445	0.019	0.304	0.005

<sup>a</sup>Average of 4 replications.

The data are presented graphically in Fig. 20 as plots of drainage time against average basis weight  $\bar{w}$ . The vertical bars show the maximum range of values at a given condition. It is seen that, for the heavier sheets, the higher the basis weight, the greater the decrease in drainage time upon addition of polymer.

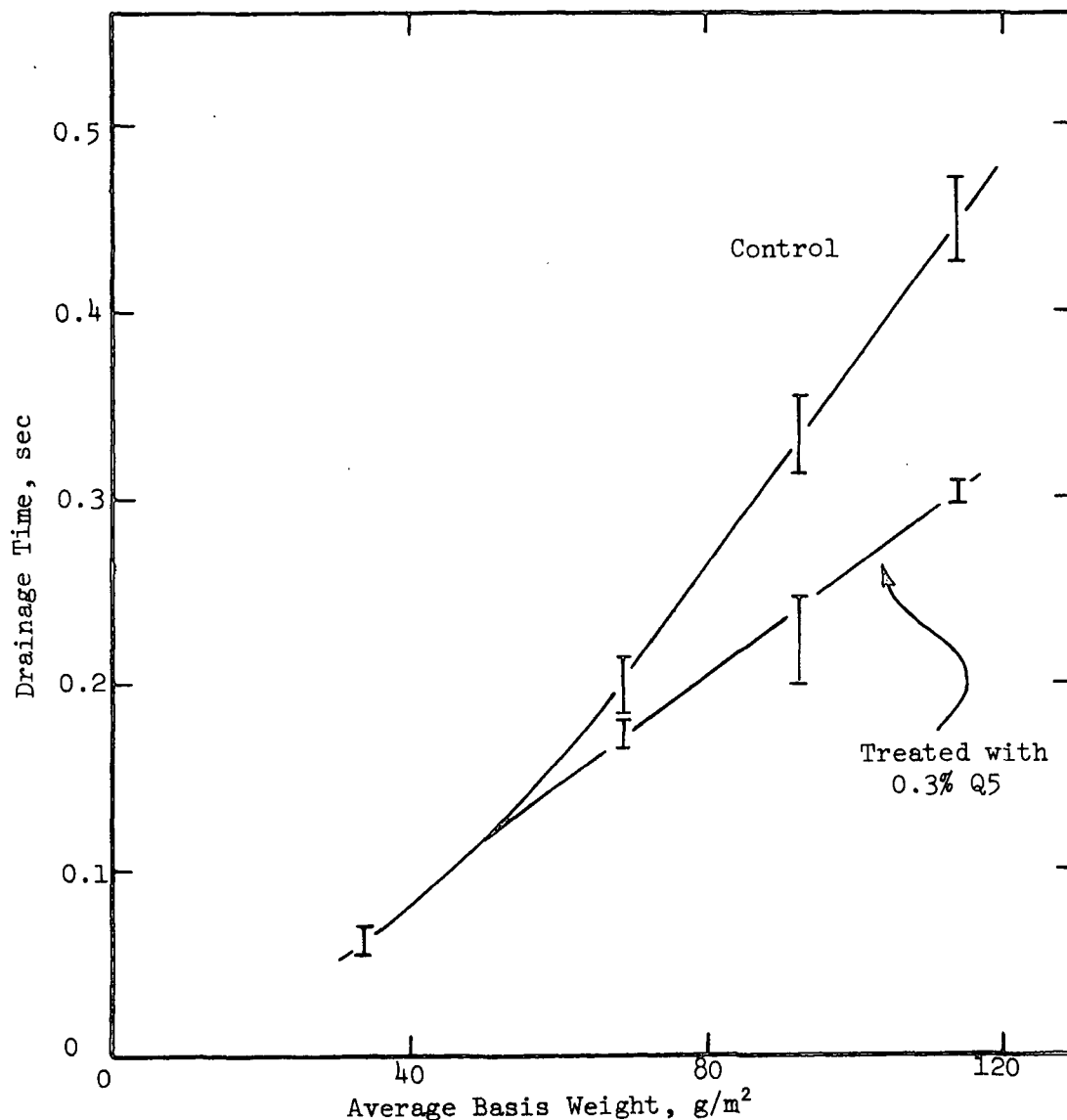


Figure 20. Variation of Drainage Time in RMA with Basis Weight.  
Pulp: No. 3 Whole. No  $\text{TiO}_2$ . Contact Time: 7.9 sec

Practically, these results mean that we will not be able to measure retention and drainage properties simultaneously on the standard ( $67.5 \text{ g/m}^2$ )

sheets. One solution is to use a higher basis weight, but this will change the relative importance of the several retention mechanisms and make comparison with previously obtained data difficult. Another alternative might be to use a furnish with a much lower freeness. Again, problems of comparison with previous work are obvious.

In order to test the correlation between drainage improvement and retention with a given polymer, the former strategy (higher basis weight) was selected. Sheets were formed with the RMA at a final basis weight of  $127 \text{ g/m}^2$  with various dosages of Q100 as a retention and drainage aid. Contact times of 7.9 and 40 sec and the usual  $\text{TiO}_2$  addition level (5%) were used. Concurrently with sheet formation the drainage times were noted and were converted to average drainage rates. The sheets were not analyzed for  $\text{TiO}_2$  retention since this information had been obtained earlier (cf. Fig. 9).

The results are shown in Fig. 21 as plots of retention and drainage rate against polymer dosage at the indicated contact times. The data for the average drainage rates are the mean of duplicate determinations. It will be recalled from the section on retention that the broad maximum in the retention curves was interpreted to be the result of two different retention mechanisms. Charge neutralization (or electrostatic patch) is thought to be the dominant mechanism at low polymer concentration and near the point of zero electrophoretic mobility. At higher concentrations, bridging by the high molecular weight polymer provides the retention. Using the same arguments for the drainage rate data, one must conclude from the position of the maxima on the concentration scale that bridging is the important mechanism of drainage enhancement with this polymer. Although the drainage rate maxima are rather narrow compared with those for  $\text{TiO}_2$  retention, they do span a range of concentrations of a factor of

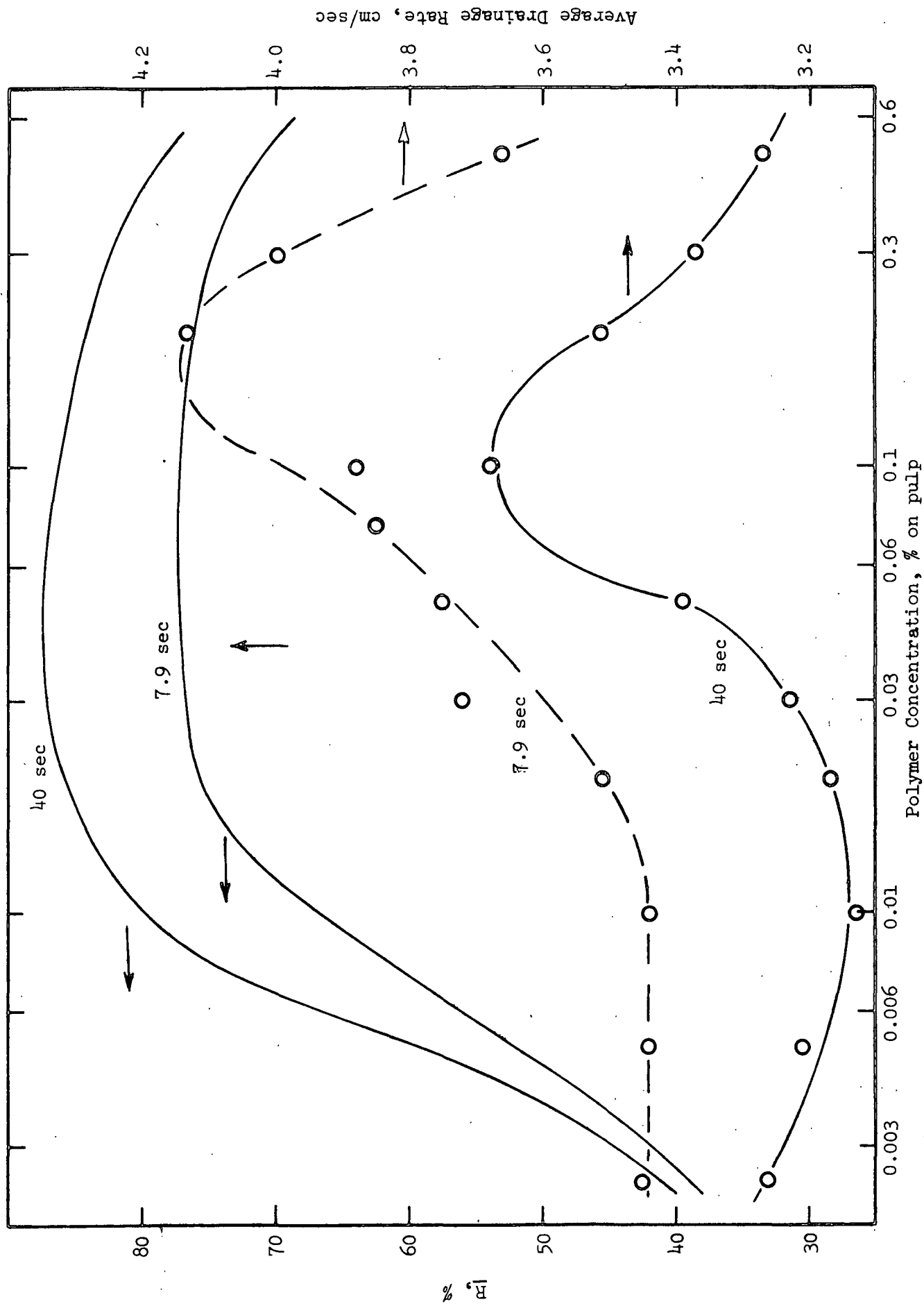


Figure 21. Correlation of Retention and Drainage Parameters on RMA. Pulp: No. 3 Whole. Polymer: Q100. Final Basis Weight: 127 g/m<sup>2</sup>. Vertical Arrow Indicates Concentration at Zero Zeta Potential

three or more. At the upper end of the concentrations examined the drainage rates decrease much more drastically than do the retention results. This rapid drop-off is similar to that found for freeness measurements of whole pulp No. 4 with the same polymer [Ref. (1), Fig. 12]. It can be speculated that the large positive zeta potentials at these dosages inhibit the drainage mechanism.

It is difficult to explain the difference in drainage rates for the two contact times. Accepting the data at face value, one is forced to conclude that the drainage rates are decreasing with increasing contact time at the same time that  $TiO_2$  retention is increasing. However, because the difference persists to extremely low polymer concentrations where there is little effect on drainage rates, and because the difference is roughly constant over most of the concentration range, it is thought more likely to be an experimental artifact. During the additional 32 sec contact time, the 40-sec experiment is being gently stirred in the deckle box. It is possible that during this time some sedimentation of fibers or fines occurs either forming a thin pad or partially plugging the wire leading to a reduced drainage rate. Experiments with classified pulp and with more vigorous stirring should lead to a better understanding of this unexplained behavior.

#### CONCLUSIONS

Polymers of moderate molecular weight and either high or low charge density produce little change in the filtration resistance from that of the untreated pulp. Polymers of high molecular weight and either high or low charge density can produce sizeable decreases in filtration resistance. From both filtration resistance and drainage time (RMA) results, it is concluded that polymer bridging is the most effective mechanism for enhancing drainage.

Decreases in hydrodynamic specific surface area resulting from the application of drainage aids correlate more closely with the corresponding changes in filtration resistance than do the changes in hydrodynamic specific volume or pulp compressibility. At the fines levels studied here ( $< 15\%$ ) the dominant factor in the improvement of drainage is the effect of the polymer in decreasing the specific surface area of the highly fibrillated fibers.

Some drainage aids can improve water removal in the press section. Polymers which are effective in enhancing drainage on the wire may be ineffective for increasing dewatering in the presses.

Polymers improve drainage on the wire appreciably only when the porosity of the sheet has decreased below some (yet to be specified) value.



## FUTURE WORK

The retention studies projected for the next time period will proceed along two parallel tracks.

## I. BASIC STUDIES

The rates and amounts of polymer adsorption onto the various components of the furnish (fiber, fines, and filler) will be determined. For this purpose radioactively-tagged polymers and fines have been prepared. This work will lead to a better understanding of the several steps in the retention process.

Fractionation of Q100 has been carried out on a preparative gel permeation chromatography column. These fractions will be used to examine further the role of molecular weight on retention. In particular, the importance of "bridging" and nonequilibrium flocculation (1) to the performance of a retention aid will be studied. The influence of the polymer "reshuffling" mechanism (25) on the retention process will also be investigated.

## II. INFLUENCE OF OPERATIONAL VARIABLES

The effect of pulp fines on retention will be studied using a classified pulp plus various levels of added fines. The relationship between the amount of fines and the optimum polymer dosage will be ascertained.

The influence of polymer feed concentration will be investigated. The RMA has been modified to permit polymer solution concentrations between 0.01 and 0.2% to be fed to the mixing tee. The effect of polymer feed concentration on "bridging" (during nonequilibrium flocculation), on the uniformity of distribution to the stock (mixing efficiency), and on the optical properties are of primary interest here.

Increased agitation in the deckle box will be studied to gain a better understanding of the effect of polymer structure on the tenacity of retention toward shearing.

The retention studies will be extended to furnishes containing filler clays to determine to what extent the findings with  $TiO_2$  can be extrapolated to such systems.

The research on Project 3276 is being coordinated with that on Project 3245, "Improving Retention of Particulate Matter when Employing Recycled White Water." The objectives of both projects concern a better understanding of the process of retention of fillers. The present project is devoted to understanding the role of polymers in retention. Project 3245 concerns the effect of recycling white water on retention using either alum or polymers as retention aids. The research on both projects is being directed so that the individual results will be mutually complementary. For example, results already obtained in Project 3245 on the retention of clay using alum will be correlated with the work described above to be performed on the retention of clay using polymers. It is anticipated that this approach will lead to a more rapid development of our understanding of the retention process.

Studies of drainage mechanisms will be continued using the drainage time measurement of the RMA. Classified pulp and classified pulp plus added fines will be used to gain a better understanding of the role of fines in drainage. The influence of polymer structure on drainage aid performance will be investigated further. Simultaneous studies of retention and drainage will indicate the correlation between the two phenomena.

#### ACKNOWLEDGMENTS

The experimental work on the rapid mixing apparatus was carried out by Norman L. Colson and Donald H. Gilbert. The measurements and analyses of filtration resistance were performed by Bruce D. Andrews. James Tierney and Orlin C. Kuehl assisted with the wet pressing experiments. Keith W. Hardacker designed and constructed the interfacing electronics for the operation of the drainage timer.

LITERATURE CITED

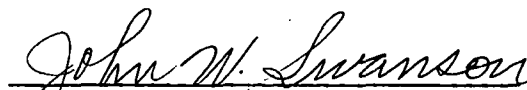
1. Stratton, R. A., and Swanson, J. W. A fundamental study of the mechanisms of action of polymers as retention and drainage aids. Progress Report One, Project 3276, Appleton, WI, The Institute of Paper Chemistry, March 10, 1976.
2. Andrews, B. D. Personal communication, 1976.
3. Moore, E. E., Tappi 59(6):120(1976).
4. Miller, J. R., Jr. Doctoral Dissertation. Appleton, WI, The Institute of Paper Chemistry, 1972.
5. Andrews, B. D. Unpublished work, The Institute of Paper Chemistry, 1975.
6. Williams, D. G., and Swanson, J. W., Tappi 49:147(1966).
7. Lodzinski, F. P. Private communication, 1976.
8. Gregory, J., J. Colloid Interface Sci. 55:35(1976).
9. Stratton, R. A. Unpublished work, The Institute of Paper Chemistry, 1976.
10. Kane, J. C., LaMer, V. K., and Linford, H. B., J. Phys. Chem. 67:1977(1963).
11. Lindquist, G. M., and Stratton, R. A., J. Colloid Interface Sci. 55:45(1976).
12. Kasper, D. R. Doctoral Dissertation. Pasadena, CA, California Institute of Technology, 1971.
13. Gregory, J., J. Colloid Interface Sci. 42:448(1972).
14. Ingmanson, W. L., and Andrews, B. D., Tappi 46(3):150(1963).
15. Andrews, B. D. Personal communication, 1976.
16. Moore, E. E., Tappi 58(1):99(1975).
17. Ingmanson, W. L., and Andrews, B. D., Tappi 42(1):29(1959).
18. Carroll, M., and Mason, S. G., Can. J. Technol. 30(12):321(1952).
19. Chang, M. Y., and Robertson, A. A., Pulp Paper Mag. Can. 68(9):T438(1967).
20. Pendrich, T. W. E., Paper 180(5):291(1973).
21. Ingmanson, W. L., and Whitney, R. P., Tappi 37(11):523(1954).
22. Poschmann, F. J., Pulp Paper Mag. Can. 69(8):59(1968).
23. Williams, D. G. Personal communication, 1976.
24. Walls, J. Personal communication, 1975.

25. Swanson, J. W., Janes, R. L., and Emery, P. H., Jr. In Proceedings of the Symposium on Man-Made Polymers in Papermaking, June 5-8, 1972, Helsinki, Finland. p. 22. Publ. 1973.

THE INSTITUTE OF PAPER CHEMISTRY



Robert A. Stratton  
Research Associate



John W. Swanson  
Director  
Division of Natural  
Materials & Systems

